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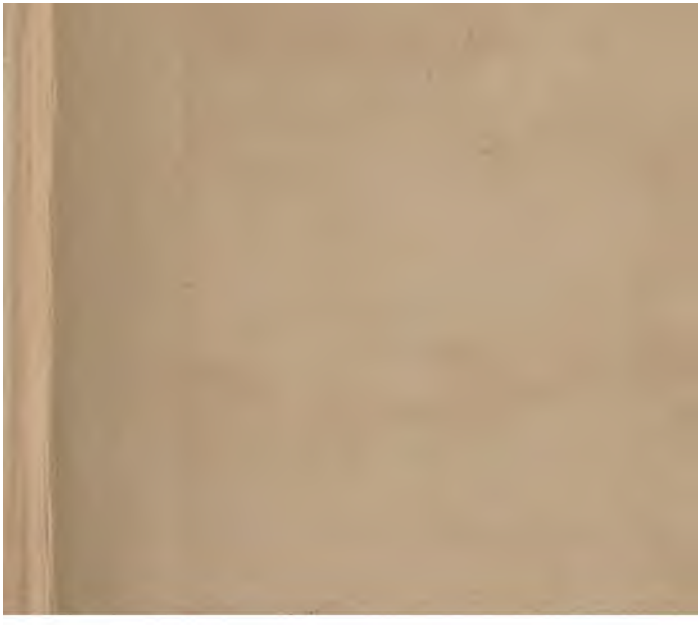

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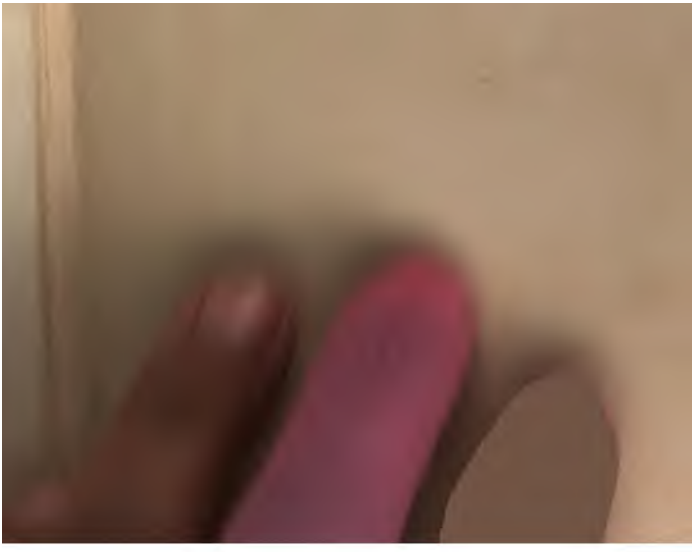

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MODERN CHEMISTRY

Theoretical

By

Sir WILLIAM RAMSAY, K.C.B., F.R.S.

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MODERN CHEMISTRY

THEORETICAL

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FIRST PART

THEORETICAL CHEMISTRY

CHAPTER I

INTRODUCTORY

Elements—Phlogiston—Discovery of Oxygen—Combining Proportions—Dalton's Laws—Gay-Lussac's Law of Volumes—Avogadro's Hypothesis—Atomic Weights—Molecular Weights—Dulong and Petit's Law—Equivalents—Isomorphism.

One of the earliest questions asked by an intelligent child is: "What is this made of?" "What is that made of?" And the answer is generally more or less satisfactory. For example, if the question relates to butter, the reply may be, "From cream." It may be explained, besides, that when cream is beaten up, or churned, the butter separates, leaving skim-milk behind. But the question has not been answered. The child may ask, "Was the butter in the milk before it was churned? or has it been made out of the milk by the churning?" Possibly the person to whom the question is addressed may know that the milk contained the butter in the state of fine globules, and that the process of churning breaks up the globules, and causes them to stick together. The original question has not really been answered; and indeed it is not an easy one to reply to. Precisely such questions suggested themselves to the people of old, and they led to many speculations.

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Elements.—One of these speculations was that things which we see around us were built up out of elements, just as a word is built up out of letters. Indeed, the word *elemens*, which is the Latin word for element, is probably derived from the letters *l*, *m*, and *n*, and involves that idea. The ancient Greeks surmised that there were four such elements—earth, water, air, and fire. But as it was obvious that some things, for instance gold and silver, did not contain either water or air, the word element was often used to signify, not the constituent of a thing, but rather a property of a thing; and it might have been said that gold partook of the properties of earth and water, because, like earth, it is not altered by being heated, and yet it can take a fluid form like water if heated hot enough. Hence the old word "element" had a double meaning; it was sometimes used in the sense of "constituent," and sometimes more in the sense of "property."

If a child is given a mechanical toy, his wish to see how it works generally leads to his taking it to bits. This is unfortunately only too easy; but it is seldom that he succeeds in putting it together again. Now, if we inquire what a piece of wood or stone is made of, we can, after a fashion, take them to bits; we may pull the wood into fibres, or we may crush the stone, and pick out the pieces that appear to differ from each other in colour, if they are large enough. But the fibres have much the same appearance as the piece of wood, and the fragments of stone, though somewhat different from each other, are still pieces of stone. The question is still to be answered, of what do wood and stone consist? It is evident that some plan must be tried by which the wood and stone will be unbuilt, as it were, and by which they will yield their constituents.

It had long been noticed that many things are greatly *changed* when heated. A piece of wood takes fire and *burns; some kinds* of stone melt; some metals, such as lead *nd iron, change* into earthy-coloured powders. Surely *ese changes* ought to lead to some knowledge of the

nature of wood, stone, and metals. It was long, however, before it was recognised that the presence or absence of air made a difference in the result of heating substances. When attention was drawn to this difference, a new suggestion was adopted. It was, that things, besides consisting of or sharing the properties of earth, water, air, and fire, also consist of, or at least are like, salt, sulphur, and mercury. Salt dissolves when put into water; so do many other things. These things must either contain a kind of salt to account for this property; or they must at least share the property of salt, in so far as they dissolve. Similarly, other things, especially metals, must either contain or share the property of mercury, seeing that they shine with the same kind of lustre; and many things resemble sulphur in so far as they burn and produce a smell in burning. And it was often imagined that when things burn, the sulphur which they contain flies away and disappears, just as ordinary sulphur, when set on fire, burns away completely, leaving nothing behind. About the middle of the seventeenth century, **Johann Joachim Becher**, a German alchemist, altered somewhat the conception that substances contain, or are like, salt, sulphur, and mercury; he imagined all things existing on the surface of the globe to contain three earths, namely the mercurial, the glassy, and the fatty, the last implying the property of being able to burn. And in the early years of the eighteenth century, Becher's pupil, **George Ernest Stahl**, who was Professor of Medicine in Jena, and later in Halle, two small German towns, made an important addition to the ancient theories, namely, that it was possible to restore the "sulphur," or the "fatty earth," as Becher called it, to things which had been deprived of it by burning, by heating them with other substances rich in that constituent.

Phlogiston.—Stahl devised a new name for this combustible constituent of substances, in order better to direct attention to his new idea; he called it "phlogiston," a word which may be translated "burnableness," for it is derived

from a Greek word signifying flame. Thus lead, which when heated in air changes to an earthy dross, or, as it was then termed, "calx," may be restored to the state of metal by heating it with charcoal powder, or with flour, or with any substance rich in "phlogiston;" that is, with any substance which is itself capable of burning. He supposed that the lead was rich in "phlogiston;" that when it changed to lead-dross, the "phlogiston" escaped; but that on heating with charcoal, the latter parted with *its* phlogiston to the lead-dross, changing it back again into lead. It is evident that this idea accounts for some of the facts observed; and it gained ground rapidly. But it had been shown by the French physician Jean Rey, by the English philosopher Robert Boyle, and others, that metals, when they changed into earthy powders on heating, gained weight; and it is at least curious that the lead, on *losing* one of its constituents, namely "phlogiston," should *gain* weight: one would have expected that weight would be lost, not gained. The way out of this difficulty was ingenious. We know, it was said, that weight is due to the attraction of the earth; now, it is not impossible that the earth may repel phlogiston, instead of attracting it; and in that case a body would grow heavier, instead of lighter, if it parts with phlogiston. Another objection to the theory was that a candle, for example, which is rich in phlogiston, goes out when made to burn under a glass shade; that is, when air is excluded. True, said the phlogistonists; that is because the phlogiston cannot escape. And because this theory gave a plausible explanation of the common phenomenon of combustion, it was widely accepted, and survived until the end of the eighteenth century.

The idea had been steadily gaining ground that knowledge was to be acquired only by trial and failure. **Francis Bacon, Lord Verulam,** at the end of the sixteenth century *wrote:* "The true kind of experience is not the *mere groping of a man* in the dark, who feels at random *to find his way,* instead of waiting for the dawn or striking

a light. . . . It begins with an ordered—not chaotic—arrangement of facts, deduces axioms from these, and from the axioms again designs new experiments." Many experiments were made on the action of heat on various things, either alone or mixed with others. **Boyle**, who introduced the word "analysis" to denote the art of discovering one substance in presence of another, and who contended for the use of the word "element" in the meaning of a *constituent* of, and not as a *property* of matter, made many such experiments, and systematically put Bacon's advice into practice. And so knowledge of facts gradually accumulated, and speculations acquired some substantial basis. To **Priestley**, a nonconformist clergyman of Birmingham, we owe the discovery of numerous gases, and **Scheele**, his contemporary, a Swedish apothecary, also enriched chemistry in this respect. The discovery of oxygen, in 1774, was made simultaneously by both of these illustrious men. It had been generally supposed that all gases, or, as they were then termed, "airs," were merely modifications of atmospheric air; and it was not uncommonly held that air, in consequence of its want of substantiality, was but one remove from nothing. **Joseph Black**, Professor of Chemistry in Edinburgh in the middle of the eighteenth century, was the first to prepare carbonic acid gas, or, as he termed it, "fixed air," in a pure state; and by determining the loss of weight on heating its compound with magnesia, to show that it was due to the escape of the gas; for he succeeded also in absorbing the gas, and reconstituting the carbonate of magnesia, which then possessed practically the same weight as it originally had. In spite of this discovery, made in 1756, the doctrine was still generally held that burning substances lost their constituent principle, "phlogiston;" and we owe to the French chemist **Lavoisier** the true explanation of the phenomenon of combustion. Lavoisier had been informed by Priestley in the autumn of 1774 of his discovery of what, according to the views then current, he termed "dephlogisticated

air;" he proceeded to repeat an experiment which had previously been made by Boyle, in heating metallic tin to redness in a sealed glass vessel; there was neither gain nor loss of weight, although the tin had been partly converted into "calx;" but on admitting air, he observed a gain in weight, nearly equal to that which the tin had gained on being calcined. The conclusion was obvious, that the gain in weight was due to the absorption of a portion of the air by the hot tin; and he subsequently showed that the gain was to be ascribed to the absorption of Priestley's "dephlogisticated air," of which Priestley had shown common air to contain about one-fifth. And in 1777 Lavoisier published the statements:—

(1) **Substances burn only in pure air.**
(2) **This air is consumed in the combustion, and the increase in weight of the substance burned is equivalent to the decrease in weight of the air.**
(3) **The combustible body is, as a rule, converted into an acid by its combination with the pure air, but the metals, on the other hand, are converted into "calces."**

Oxygen.—This last statement explains the name which he gave to Priestley's and Scheele's gas, namely *oxygen*, a word derived from two Greek words, signifying "acid-producer." The compounds of this substance he termed "oxides;" and it is to him that we owe the system of nomenclature now generally in use. Before the end of the century, the doctrines of Lavoisier had gained almost universal acceptance.

The word "analysis," as has been stated, was suggested by Boyle, to signify the ascertaining the composition of substances. Attempts were made by him, and by other chemists, especially by Black, to perform quantitative analyses during the seventeenth and the first half of the eighteenth centuries. Priestley and Scheele tried to find the relative proportions of oxygen in air with partial success;

but it was not until Lavoisier had convinced most chemists that oxygen was a substance, and not the negation of one, like the absence of phlogiston, that serious attention was directed to accurate determinations of quantity. And towards the end of the eighteenth century fairly trustworthy data began to accumulate.

Combining Proportions.—It became evident, chiefly owing to the work of two German chemists, **Wenzel** and **Richter**, that when an acid, such as vitriol or vinegar, is mixed with a base, such as potash, and neutralised, as the expression runs—that is, rendered incapable of changing the colour of certain vegetable extracts and deprived of its sharp taste—the same weight of base was always required to neutralise the same weight of acid. And other examples of apparently constant proportions between the constituents of substances had also been observed. But the processes of analysis were very imperfect, and the results by no means always concordant; and there was some ground for the statement made by Count **Berthollet**, a contemporary of Lavoisier, in his *Researches on the Laws of Affinity*, published in 1803, that the composition of chemical compounds was variable, and not constant; that, in fact, it depended on circumstances, such as the proportions of the substances present, on the temperature, on whether the substance produced was an insoluble solid, and so on. Berthollet's statement was disputed by his countryman **Proust**, who, by fairly accurate analyses, carried out during eight years of controversy, proved the truth of the doctrine of constant proportions. But in the course of his work, he found that in certain cases two elements form more than one compound with each other; for example, tin combines with oxygen in two proportions, each of them fixed and constant; and iron forms similarly two compounds with sulphur. Perhaps the most exact experiments which had at that time been made were those due to the **Hon. Henry Cavendish**, who having *discovered that* water was composed of oxygen in union with *another gas*, to which the name "hydrogen" was subse-

quently given, determined the proportion of these constituents with very great accuracy. He found that two volumes of hydrogen invariably combine with one volume of oxygen to produce water, neither hydrogen nor oxygen being left over. Owing, however, to the method of expressing the composition of compounds, no relation was evident between the proportions of the constituents. Thus Proust expressed the results of his determination of the composition of the two oxides of tin and of copper in parts per hundred :—

	Suboxide of copper.	Protoxide of copper.	Suboxide of tin.	Oxide of tin.
Metal . . .	86.2	80	87	78.4
Oxygen . . .	13.8	20	13	21.6
	100.0	100	100	100.0

Had he calculated by simple proportion how much oxygen is combined with the same weight of copper and tin in each case, he would have found that the ratio of the oxygen in the suboxide of copper to that in the protoxide is as 13.8 to 21.5 ; and in the two oxides of tin as 13 to 24. The correct figures are :—

	Suboxide of copper.	Protoxide of copper.	Suboxide of tin.	Oxide of tin.
Metal . . .	88.8	79.9	88.2	78.9
Oxygen . . .	11.2	20.1	11.8	21.1
	100.0	100.0	100.0	100.0

The ratio should be as 1 to 2 in each case ; and the fact that Proust did not remark this is to be ascribed partly to his method of stating his results, and partly to the inaccuracy of his analyses.

Attention was first drawn to the existence of simple proportionality between the amounts of one element forming more than one compound with another by John Dalton, a Manchester schoolmaster, in 1802 and the next succeeding

years. In the year named, he described experiments "On the proportion of the several gases in the atmosphere;" and he then stated: "The elements of oxygen may combine with a certain portion of nitrous gas, or with twice that portion, but with no intermediate quantity." And he later illustrated the same fact by considering the composition of two compounds of carbon with hydrogen, marsh gas, and olefiant gas, the former of which contains twice as much hydrogen as the latter, proportionally to the same weight of carbon.

The laws relating to the proportions in which various elements combine are therefore usually called *Dalton's Laws*; they are:—

Dalton's Laws.—*The law of definite proportions:*—**When two or more elements combine with each other to form a compound, they combine in constant proportions by weight.**

The law of multiple proportions:—**When two elements form more than one compound with each other, they combine in simple multiple proportions.**

Thus, if A and B are definite weights of two elements, the proportions in which they combine will be A with B; or A with 2B; or A with 3B; or 2A with B; or 2A with 3B; or 3A with 2B, &c.

But Dalton not merely stated these facts; he devised a theory with a view to explaining them; he revived and gave definiteness to the ancient conception that all substances which we see around us consist of atoms. This idea is at least as ancient as 400 B.C., and is to be found in the writings of the Greek philosophers. The theory, in the form which Dalton gave it, is as follows: All compounds consist of atoms of elements united with each other. An atom is an indivisible (literally "uncuttable") particle, or, more correctly, a particle which resists division. Each atom has its own definite weight; but as there is no apparent *means of determining* this weight (for atoms are *inconceivably small*), we must be contented in determining their

weights relatively to each other. This we can do by ascertaining the proportion in which they exist in their compounds. Thus, knowing that water consists of oxygen in combination with hydrogen, if the smallest particle of water consists of one atom of each element, the relative weights of the atoms will be found by discovering the proportions by weight in which these elements are combined with each other. Now, it is found that 8 parts by weight of oxygen and 1 part of hydrogen by weight combine to form 9 parts by weight of water; hence an atom of oxygen is eight times as heavy as an atom of hydrogen; and an atom of water is nine times as heavy.

We must beware of confusing this theory with the facts on which it is founded; indeed, Dalton's contemporaries, while accepting the facts, refused in many cases to accept his theory. Sir Humphry Davy used the word "proportion" in place of the word "atom;" and Dr. Wollaston preferred the word "equivalent." And even granting the existence of atoms, the problem of determining their relative weights is not so simple as would at first sight appear. For how is it possible to know which of several compounds is the one containing only one atom of each element? The two compounds of carbon with hydrogen by means of which Dalton illustrated his law will furnish a good example of this difficulty. While one of them, marsh-gas, consists of one part by weight of hydrogen in combination with three parts of carbon, the other consists of one part of hydrogen, in union with six parts of carbon. Which of these two contains one atom of each element? If the former, then the atom of carbon is three times as heavy as the atom of hydrogen; if the latter, it is six times. Dalton was quite aware of this difficulty, but could devise no means of overcoming it, and the numbers which he adopted were only provisional.

The difficulty was solved chiefly by the experimental work of Joseph Louis Gay-Lussac, Professor of Chemistry in the École Polytéchnique in Paris, and by P. L. Dulong

and T. A. Petit, Director of, and Professor in, the same school. The attention of Gay-Lussac having been directed by the celebrated explorer Humboldt to the fact that water is formed by the union of one volume of oxygen with two volumes of hydrogen gas, he followed it up by the discovery that other gases unite in very simple proportions by volume. Of this we shall see many instances hereafter.

Gay-Lussac's Law of Volumes.—Stated in the form of a law, Gay-Lussac's discovery was:—**The weights of equal volumes of both simple and compound gases are proportional to their combining weights** (or, to use Dalton's term, their atomic weights), **or to rational multiples of the latter.** This law appeared as if it ought to have some simple relation to Dalton's laws; but there is an apparent difficulty in reconciling them, which was surmounted in 1811 by **Amadeo Avogadro**, Professor of Physics in Turin. The difficulty is this:—

Imagine a given volume, say a cubic inch, to be filled with oxygen; suppose it to contain a very large but unknown number of atoms of oxygen, which we will call n. This oxygen, if mixed with twice its volume of hydrogen, or two cubic inches, and made to combine with it (which can be done by heating the mixture with an electric spark), yields nothing but water; and neither of the gases remains uncombined in excess. Let us suppose that n atoms of oxygen combine with $2n$ atoms of hydrogen; and as water also, according to Dalton, consists of atoms, there will be n atoms of water formed by their union. But experiment shows that the water, in the state of water-gas or steam, has a volume equal to that of the hydrogen from which it was formed; that is, n atoms of water-gas inhabit a volume equal to that inhabited by $2n$ atoms of hydrogen. From this it would appear that equal volumes of gases do not contain equal numbers of atoms; and while some chemists supposed, with Dalton, that water consists of one atom of oxygen in union with one atom of hydrogen, others imagined that two atoms of hydrogen were present for each

atom of oxygen, basing their conclusions on the fact that two volumes of hydrogen combine with one volume of oxygen, and considering it probable that equal volumes of gases contain equal numbers of atoms. This last probability was maintained by **Avogadro**, and he defended his doctrine by the following suggestion.

Avogadro's Hypothesis.—Substances consist of two kinds of particles, each of which has been termed an atom by Dalton. But they are in reality different. The smallest particle, or, as Avogadro named it, *molecule*, of water, consists of three atoms, two of hydrogen and one of oxygen. But hydrogen *gas* and oxygen *gas* also consist of molecules, each of them containing two atoms. The act of union of these elements is to be regarded not as a case of combination of atoms, as Dalton supposed, but rather as an exchange of partners; the atom of oxygen leaving the other atom with which it had been combined, and uniting with two atoms of hydrogen, each of which had similarly left its partner. Thus n molecules of oxygen exchange partners with $2n$ molecules of hydrogen, and form $2n$ molecules of water-gas; but whereas the molecules of oxygen and hydrogen each contain two atoms, those of water-gas contain three. And this explanation is consistent with the facts; for while $2n$ molecules of hydrogen and n molecules of oxygen, containing together $6n$ atoms, react to form $2n$ molecules of water-gas, the latter also contains $6n$ atoms, for each molecule of water-gas contains three atoms.

Using the symbols H and O for one atom of hydrogen and one atom of oxygen respectively, Dalton's idea of the combination was—

$$H + O = HO.$$

On the assumption that equal volumes of the gases contain equal numbers of atoms, the equation becomes—

$$2H + O = H_2O.$$

Lastly, on Avogadro's hypothesis, that the action is one

between molecules of hydrogen and molecules of oxygen, each containing two atoms, the equation is:—

$$2H_2 + O_2 = 2H_2O.$$

Granting Avogadro's hypothesis, the relative weights of the atoms can be ascertained. For, as oxygen is 16 times as heavy as hydrogen, and as equal volumes of these gases contain equal numbers of molecules, and moreover as each molecule consists of two atoms, it follows that an atom of oxygen is 16 times as heavy as an atom of hydrogen.

Atomic Weight.—This is usually expressed by the phrase—**the atomic weight of oxygen is** 16; for the atomic weight of hydrogen, being the smallest known, was taken as the unit.

The relative weight of a molecule can also be calculated; as an instance, let us calculate the molecular weight of water-gas. Experiment shows that a given volume of water-gas is 9 times as heavy as an equal volume of hydrogen at the same temperature and pressure; again, equal volumes of gases contain equal numbers of molecules; therefore a molecule of water-gas is 9 times as heavy as a molecule of hydrogen. But a molecule of hydrogen consists of two atoms; consequently a molecule of water-gas is 18 times as heavy as an atom of hydrogen.

Molecular Weights.—This is usually expressed by saying that the molecular weight of water is 18; and inasmuch as it consists of two atoms of hydrogen in union with one atom of oxygen, the weight of a molecule of water-gas is equal to the sum of the weights of the atoms composing it; for, $(2 \times 1) + 16 = 18$.

Dulong and Petit's Law.—Let us now consider the discovery of Dulong and Petit, already alluded to. In 1819 they made the announcement that the atoms of simple substances, or elements, have equal capacity for heat. It must be explained that equal weights of different substances require different amounts of heat to raise them

through the same interval of temperature. Thus, if the amount of heat required to raise the temperature of a gram of water from, let us say, 0° C. to 100° C. be taken as unity, it is found that only one-ninth of that amount is required to raise an equal weight of iron through the same range of temperature. Or, in other words, while the specific heat of water is 1, that of iron is $\frac{1}{9}$, or in decimals, 0.112. The quantity of heat necessary to be imparted to one gram of water to raise its temperature through 1° C. is termed a **heat-unit**, or **calory**; but sometimes the unit is chosen one hundred times as large, and represents the heat required for a rise of temperature from 0° to 100°; and the French make use of a unit one thousand times that of the smallest unit. Dulong and Petit's discovery was, that if weights of the solid elements be taken proportional to their atomic weights, equal amounts of heat must be imparted to them in order to raise them through the same interval of temperature. The following table illustrates this fact, and exhibits some of the results obtained by Dulong and Petit:—

Element.	Atomic weight.	Specific heat.	Atomic heat.
Bismuth . . .	208	0.0288	6.0
Lead . . .	207	0.0293	6.0
Gold . . .	197	0.0298	5.8
Platinum . .	195	0.0314	6.1
Silver . . .	108	0.0570	6.1
Copper . . .	63	0.0952	6.0
Iron	56	0.1138	6.4
Sulphur . . .	32	0.1776	5.7

If the specific heat be taken as the heat required to raise the temperature of one gram of each of these substances through one degree, compared with that required for one gram of water, the atomic heats of bismuth, lead, gold, and the others represent the heats required for 208 grams of bismuth, 207 grams of lead, and so on. It is evident that they are all nearly equal. It should follow that the

specific heat of solid hydrogen must be also 6, since the atomic weight is taken as 1.

These facts, though clearly indicating the numbers which should be taken for the atomic weights of the elements, were neglected, until renewed attention was called to them in 1858 by **Cannizzaro**, still Professor of Chemistry at Rome. He pointed out that all that can be gained from the analysis of a compound, for example an oxide, is the "equivalent" of the element. And as an element, such as iron, often forms more than one compound with other elements, let us say oxygen or chlorine, it therefore may possess more than one equivalent. But granting the atomic hypothesis, its atom can have only one definite weight. That atomic weight may, however, be inferred from its specific heat, or from the density of its gaseous compounds. Let us consider a concrete instance of each of these methods.

The analysis of two of the oxides of iron leads to the following results:—

	Ferrous oxide.	Ferric oxide.
Iron	77·77	70.00
Oxygen	22.22	30.00
	99·99	100.00

Equivalent.—Now, 1 gram of hydrogen combines with 8 grams of oxygen in water;[1] and 8 is therefore chosen as the equivalent of oxygen; for the definition of an equivalent is **that amount of an element which will combine with or replace one part by weight of hydrogen.** In ferrous oxide, since 22.22 grams of oxygen combine with 77.77 grams of iron, 8 grams of oxygen will combine with $\frac{77.77 \times 8}{22.22} = 28$ grams of iron; and in ferric oxide, 8 grams of oxygen are in combination with $\frac{70 \times 8}{30} = 18.66$ grams of iron. Thus the equivalent

[1] *This statement is to be taken as merely approximate; see pp. 74 and 75.*

of iron in ferrous oxide is 28, and in ferric oxide 18.66. The question now arises, What is the atomic weight of iron? We have seen that the specific heat of iron is 0.1138; and we know that the specific heat of solid hydrogen is probably 6. And as the specific heats of elements are inversely as their atomic weights, we have the proportion—

Specific heat of iron.		Specific heat of hydrogen.		Atomic weight of hydrogen.		Atomic weight of iron.
0.1138	:	6	::	1	:	52.7

The number 52.7 is nearly 2×28, and nearly 3×18.66; these products give 56; and it must be remembered that Dulong and Petit's law is not absolute, but merely an approximation; hence 56 is accepted as the true atomic weight of iron.

The element sulphur forms a compound with hydrogen which has the following composition:—

Sulphur	94.12 per cent.
Hydrogen	5.87 „
	100.00

The gas is 17.1 times as heavy as hydrogen; and this means that a molecule of hydrogen sulphide is 17.1 times as heavy as a molecule of hydrogen. But a molecule of hydrogen is believed to consist of two atoms; hence a molecule of hydrogen sulphide is 34.2 times as heavy as an atom of hydrogen. Now, if this gas consists of one atom of hydrogen in combination with one atom of sulphur, then the atomic weight of sulphur will be the same as its equivalent, viz., $\frac{94.12}{5.88} = 16$; but if it contain two atoms of hydrogen, then the atomic weight of sulphur will be $\frac{94.12 \times 2}{5.88} = 32$. The first hypothesis is impossible, for then the *molecular* weight of hydrogen sulphide would

16 + 1 = 17; whereas, it has been found to equal 34.2; but if two atoms of hydrogen are present in sulphide of hydrogen, the molecular weight is 32 + 2 = 34; and this is nearly the same as the number found, viz., 34.2. It is, however, still possible that hydrogen sulphide consists of two atoms of hydrogen in union with two atoms of sulphur, in which case the atomic weight of sulphur might still be 16; but many other gaseous or gasifiable compounds of sulphur are known, and in none of them is the molecular weight such that they could be supposed to contain less than 32 parts of sulphur for each part of hydrogen, or its equivalent of another element. It is consequently regarded as improbable that the atomic weight of sulphur is less than 32; and that 32 is the correct number follows also from the determination of its specific heat.

Isomorphism.—A third method of arriving at the correct atomic weight of an element was suggested in 1819 by **Eilhard Mitscherlich,** then Professor in Berlin. When two substances crystallise in the same crystalline form, they are said to be "isomorphous" with each other. It is often the case that such compounds are similar chemically; that is, they may contain the same number of atoms, and may also closely resemble each other physically. Thus, there is a large class of compounds, named "alums," which are sulphates of two metals. Ordinary alum is a sulphate of aluminium and potassium; it crystallises in eight-sided regular figures, termed "octahedra." When the rare metal gallium was discovered, it was found to form an "alum;" it gave a sulphate of gallium and potassium, crystallising in octahedra, and similar in properties to ordinary alum. Now, Mitscherlich's statement was, that when one element takes the place of another in an isomorphous crystal of the same chemical character, the substitution occurs so that one atom of the one replaces one atom of the other. Hence, if the atomic weight of the one element is known, the weight of *the other element* which replaces it will be proportional to *its atomic* weight. In the case above mentioned, it was

found that 27.1 parts by weight of aluminium were replaced by 69.9 parts of gallium; and as it was known from experiments such as those previously described that the atomic weight of aluminium is 27.1, it follows that 69.9 is the atomic weight of gallium. But care is necessary in using this indication of the atomic weight; for it may happen that two compounds may contain the same number of elements in the same proportions, and have a similar crystalline form; and yet Mitscherlich's law may not be applicable.

CHAPTER II

Gaseous and Osmotic Pressure—Boyle's, Gay-Lussac's, Pfeffer's, and Raoult's Laws.

If we grant, in accordance with modern views, that matter consists of minute particles, termed molecules, it must also be allowed that the distance between these ultimate particles must be very different, according to whether the matter is in the solid, or liquid, or in the gaseous state. Thus, a cubic centimeter of water at 100° expands, when it is boiled into steam of the same temperature, to 1700 cubic centimeters; and a cubic centimeter of oxygen, measured at its boiling-point, −182°, boils into 266 cubic centimeters of oxygen gas of the same temperature. In changing its state, therefore, from liquid or solid to gas, matter undergoes a great alteration of volume. It is accordingly to be expected that the molecules of a gas, being at so much greater a distance from each other than the molecules of a solid or liquid, should yield more readily to pressure, and should decrease in volume when the pressure is raised, much more than solids or liquids. It is also found, as appeared probable, that the expansion of a gas is much greater than that of a solid or a liquid, by a definite rise of temperature.

Boyle's Law.—The law relating to the compressibility of gases was discovered by Boyle. It is, that **if temperature be kept constant, the volume of all gases *is inversely* as the pressure.** Thus, if the pressure of the atmosphere, which is equal to 1033 grams on each square

centimeter of the earth's surface at sea-level, or approximately 15 lbs. on each square inch, be doubled, the volume of a given weight of air, or of any other gas, will be halved; on trebling the pressure the volume is reduced to one-third, and so on. As the length of a column of mercury, one square centimeter in cross-section, must be 76 centimeters in order that its weight shall be 1033 grams, 76 centimeters is taken as the "normal" height of the barometer. And if the height of the mercury in a gauge or "manometer" is 152 centimeters, the pressure which produces that rise in the mercurial column will halve the volume of a gas exposed to it.

Gay-Lussac's Law.—The law connecting the volume of a gas with the temperature was discovered by Gay-Lussac, and independently by Dalton; but it is generally attributed to the former chemist. It is:—**Provided pressure be kept constant, the volume of a gas, measured at 0° C., increases by $\frac{1}{273}$, for each rise of 1°.** Or 1 volume of gas at 0° will become 1.00367 volume at 1°; 1.0367 volume at 10°; 1.367 volume at 100°, and so on. Generally stated, if t stand for a temperature, 1 volume of gas will become $1 + 0.00367t$ when heated from 0° to that temperature.

A third law may be deduced from these two; it is, that **if the volume of a gas be kept constant, the pressure of a gas will increase $\frac{1}{273}$ of its initial value at 0° for each rise of 1°.** This is evident from the following consideration:—Suppose that 1 volume of a gas is heated from 0° to 1°; the volume will increase to 1.00367 volume. To reduce the volume again to its initial value, 1, the pressure must be raised by 0.00367 of its original amount. If the initial pressure corresponded to that of 76 centimeters of mercury, it would have to be increased to $76 + (76 \times 0.00367)$ centimeters, or to *76.279 centimeters* in order that the gas should resume *its original volume* of 1. The same consideration will *hold if the gas is* cooled instead of being heated; but

of course in that case the pressure will be reduced, instead of being raised. It follows from this, that if the temperature could be reduced to 273 below 0° C., the gas would exert no pressure. This temperature, $-273°$, is termed "absolute zero." As a matter of fact, so low a temperature has never been reached; and, moreover, it is certain that all gases would change to liquids before that temperature was attained. But it serves as the starting-point for what is termed the "absolute scale of temperature." Gay-Lussac's law may therefore be stated thus:—**The volume of a gas at constant pressure increases as the absolute temperature**; and its corollary, thus:—**The pressure of a gas at constant volume increases as the absolute temperature.** For 0° C. corresponds with 273° on the absolute scale; and 273 volumes of gas will become 274, if the temperature is raised from 273° absolute to 274° absolute. Similarly, the pressure of a gas will increase in the proportion 273 : 274 if the absolute temperature is increased from 273° to 274°.

Pressure Proved by Diffusion.—When a solid is dissolved in a liquid, as, for example, sugar in water, the particles of sugar—its molecules—must obviously be separated from each other to a greater or less extent, according as much or little water be added. And it has been noticed that if the sugar be placed in the water, and not stirred up, the sugar will dissolve at the bottom of the vessel, and the strong solution of sugar will slowly mix up with the upper layer of water, and in course of time be equally distributed through the water; just as a heavy gas, such as carbonic acid gas, if placed in an open jar, will gradually escape into the lighter air above it. This process of mixing of two liquids or gases is termed "**diffusion.**" It is now generally held that the pressure of a gas on the walls of the vessel which contains it is produced by the impacts of its molecules against the walls; and as the molecules are extremely numerous, and in a state of very rapid motion, they escape from an open vessel; so the

even a heavy gas, like carbon dioxide, will escape upwards into a lighter gas; and similarly, a light gas, like hydrogen, will escape downwards into a heavy gas, owing to the unceasing motion of its molecules. The fact that the molecules of sugar, which, by the way, becomes itself a liquid when dissolved in water, travel upwards, and diffuse through the lighter water, shows that they too are in motion; but the slowness of the diffusion, compared with the rate of diffusion of a gas, indicates that their motion is much impeded by the molecules of water, with which they are constantly coming into collision. And just as the motion of the molecules of a gas produces pressure, and causes the gas to escape through an opening, so the motion of the molecules of sugar, which causes them to rise through water against the attraction of the earth, may be taken to imply that they also exert a kind of pressure. But the molecules of water, with which the molecules of sugar are mixing, must also be held to exert pressure of the same kind, since they disperse themselves through the molecules of sugar. How is it possible to distinguish the pressure due to the sugar from that due to the water? A parallel case with gases will help us to reply to this question.

Dalton's Law of Partial Pressures.—Suppose a vessel of one litre capacity to be filled with oxygen gas at 0°, and under the atmospheric pressure of 76 centimeters of mercury. The oxygen will exert pressure on its walls equal to that of the atmosphere, for the vessel may be placed in communication with the atmosphere, in order to equalise pressure, before it is closed. Now let half a litre of hydrogen be introduced by means of a force-pump. As temperature and volume remain the same, the pressure will be increased to 76 cms. + 38 cms. Introduce another half-litre of hydrogen, and the initial pressure will be doubled; it will now be 152 cms. Let another litre of hydrogen be introduced, and the initial pressure will be trebled. We might introduce a third gas, say nitrogen, into the vessel, and the pressure would be increased proportionately to the quan-

tity introduced. Each constituent of the gaseous mixture, accordingly, exerts pressure on the walls of the containing vessel proportionally to its relative amount. For example, the pressure of the nitrogen of the oxygen and of the argon in air is proportional in each case to the amounts of these constituents, viz., oxygen, about 21 per cent.; nitrogen, 78 per cent.; and argon, 1 per cent. This statement is known as **Dalton's law of partial pressures.** If the pressure of the air is 76 cms., that of the nitrogen is $\frac{78}{100} \times 76$; of the oxygen, $\frac{21}{100} \times 76$; and of the argon, $\frac{1}{100} \times 76$ cms. In the case of liquids, however, such a method fails. For while in some instances the volume of a solution is nearly equal to that of the solvent, plus that of the dissolved substance, in others the volume is less, and in a few instances greater.

A device has, however, been discovered, by which it is possible to measure the partial pressure of the dissolved substance; and again an example will first be given from the behaviour of gases. The rare metal palladium is permeable at high temperatures by hydrogen, but not by other gases. Now, if a vessel made of palladium be filled with a gas that cannot escape through its walls—for example, with nitrogen at atmospheric pressure—equal to that of 76 cms. of mercury—and at a high temperature, say 300° C.; and if it be then surrounded with hydrogen gas, also at atmospheric pressure, the pressure of the gases in the interior of the vessel will rise to two atmospheres, owing to the entry of hydrogen through the walls, which are permeable to that gas alone. The mercury in the gauge connected with the palladium vessel will rise, until it stands at a height of 76 cms., showing that the original atmospheric pressure has been doubled. As there is no opposition to the passage of the hydrogen inwards or outwards through the walls of the vessel, hydrogen will enter until the pressure of the hydrogen in the interior is equal to that on the exterior of the vessel. But the nitrogen cannot escape, hence it exerts its original pressure of 76 cms. of mercury.

Osmotic Pressure.—The partial pressure of the dis-

solved substance in a solution has been measured by a similar plan, devised by the German botanist **Pfeffer.** It was necessary for this purpose to discover a "semi-permeable membrane," through the pores of which water could pass freely, but which would be impermeable to the dissolved substance. A slimy precipitate, produced by adding potassium ferrocyanide to copper sulphate, is not permeated by dissolved sugar, though water freely penetrates it. But a diaphragm of this nature is far too tender to withstand any pressure. Pfeffer succeeded in depositing the slimy ferrocyanide of copper in the interior of the walls of a pot of porous unglazed earthenware, and so constructing a vessel which could be closed with a glass stopper, with the help of cement. The stopper, which was hollow, was placed in connection with a gauge containing mercury; and after the pot and stopper had been filled with a solution of sugar, the stopper was connected with the gauge, which thus registered the pressure upon, and consequently exerted by, the liquid. The pot was then immersed in a large vessel of water, which could be heated to any desired temperature, not so high as to soften the cement. It was found that the water slowly entered the pot, and consequently raised the mercury in the gauge; but after a certain quantity had entered, the ingress of water stopped, and the pressure ceased to rise.

The pressure thus raised has been termed "osmotic pressure." The numbers which follow were obtained by Pfeffer:—

Concentration.	Pressure.	Ratio.
1 per cent.	53.5 cms.	53.5
2 ,, ,,	101.6 ,,	50.8
4 ,, ,,	208.2 ,,	52.1
6 ,, ,,	307.5 ,,	51.3

When a gas occupying a certain volume is increased in *quantity by pumping* in an equal volume of gas, it is clear *that the number of* molecules in the volume is doubled; *and experiment shows* that, in accordance with Boyle's law,

the pressure is doubled. The concentration of a solution is expressed by the weight of dissolved substance in 100 parts of the solution; and it is evident from Pfeffer's numbers that, on doubling the number of molecules of sugar in a given volume of the solution, the osmotic pressure is also doubled. The osmotic pressure, in fact, increases directly as the concentration, exactly as with gases.

Pfeffer also made experiments at different temperatures. Owing to the softening of the cement with which the semi-permeable pot was closed, he was not able to use high temperatures; but some of his results are given below:—

Temperature C.	Temperature Abs.	Pressure.	Pressure Calculated.
14.2° + 273	= 287.2°	51.0 cms.	51.0 cms.
15.5° „	= 288.5°	52.1 „	51.2 „
32.0° „	= 305.0°	54.4 „	54.1 „
36.0° „	= 309.0°	56.7 „	54.9 „

The results are meagre, but, so far as they go, in reasonably good accord. Experiments of this kind have seldom been made, owing to the difficulty in preparing satisfactory membranes. The calculation has been made on the assumption that the osmotic pressure, like the gaseous pressure, increases directly as the absolute temperature.

A striking proof of the correctness of the analogy between osmotic and gaseous pressure is derived from the following consideration: A gram of oxygen gas, measured at 0° C. and 76 cms. pressure, has been found to occupy 699.4 cc.; now, 32 grams of oxygen form a gram-molecule, for the atomic weight of oxygen is 16, and there are two atoms of oxygen in a molecule of the gas, as we have seen on p. 13. The volume of 32 grams is accordingly $699.4 \times 32 = 22{,}380$ cc. The simplest formula for cane-sugar is $C_{12}H_{22}O_{11}$, and as the atomic *weight of* carbon is 12, the molecular weight of sugar is *at least* $(12 \times 12) + (22 \times 1) + (11 \times 16) = 342$. If it

were possible for cane-sugar to exist in the state of gas, it might be expected that 342 grams in 22,380 cc. would exert the same pressure as 32 grams of oxygen, viz., 76 cms., since 342 grams of sugar are likely to contain as many molecules as 32 grams of oxygen. But sugar chars when heated, and decomposes. However, it is possible to calculate, by means of Boyle's and Gay-Lussac's laws, the pressure which a 1 per cent. solution of sugar ought to exert at 14.2° C. If there were 223.8 grams in 22,380 cc., the solution would be one of 1 per cent. And the pressure which it should exert would be $\frac{223.8}{342} \times 76$, or 51.66 cms. at 0° C., or 273° Abs. And at 14.2° C., or 287.2° Abs., this pressure should be increased in the proportion 273 : 287.2; giving a theoretical pressure of 52.5 cms.; the actual pressure measured was 51 cms.—a fairly close approximation. It may, therefore, be taken that sugar in solution in water exerts the same osmotic pressure on the walls of a semi-permeable vessel, as the same number of molecules would do, if it were in the state of gas, occupying the same volume, and at the same temperature.

Experiments with semi-permeable diaphragms are very difficult; the diaphragm seldom receives sufficient support from the pipe-clay walls of the pot, and is usually torn when the pressure rises to even a very moderate degree. But it is not necessary to attempt such measurements; for the Dutch chemist, **J. H. van't Hoff**, now Professor of Physical Chemistry in Berlin, pointed out in 1887 that very simple relations exist between the osmotic pressure of solutions and the lowering of the freezing-point of the solvent, due to the presence of the dissolved substance, and also the rise of boiling-point of the solvent, produced by the same cause. A proof of this connection will not be *attempted here, but* the facts may be shortly stated.

Measurement of Osmotic* Pressure by Lowering *of Freezing-point.—All pure substances have a

perfectly definite melting-point; thus, ice melts at 0° C., sulphur at 120°, tin at 226°, lead at 325°, and so on. These temperatures are also the freezing-points of the liquids, provided some of the solid substance is present. If this is not the case, then it is possible to cool the liquid below its freezing-point without its turning solid. Accordingly, water freezes at 0° if there is a trace of ice present; melted tin solidifies at 226° if there is a trace of solid tin added to the cooled liquid; and if, for example, water be cooled without the presence of ice, until it has a temperature lower than 0°, say 0.5° below 0°, on addition of a spicule of ice a number of little crystals of ice begin to form in the liquid and the temperature rises to 0°. But if there is some substance dissolved in the liquid, as, for example, sugar in the water or lead in the tin, then the freezing-point is lowered below that of the pure substance. And when the solvent freezes, in general the solid consists of the solid solvent, none of the dissolved substance crystallising out with it. It is owing to this fact that travellers in Arctic regions manage to get water to drink; for the ice from salt water is fresh, and when melted yields fresh water.

It has been observed that with the same solvent the freezing-point is lowered proportionally to the amount of dissolved substance present, provided the solution is a dilute one. Thus, a solution of cane-sugar in water, containing 3.42 grams of sugar in 100 grams of the solution, froze at 0.185° below zero; and one containing half that quantity, 1.71 grams, froze at 0.092° below zero. Again, the same lowering of the freezing-point is produced by quantities proportional to the molecular weights of the dissolved substances. Malic acid, an acid contained in sour apples, has the molecular weight 134, while it will be remembered that the molecular weight of cane-sugar is 342. Now, a solution of 1.34 grams of malic acid in water, made up with water so that the whole solution weighed 100 grams, froze at 0.187° below zero, a number almost identical with that found for sugar.

Solvents other than water may also be used; but in that case the lowering of the freezing-point is different. Acetic acid, which is vinegar free from water, is often employed; so also is benzene, a compound separated from coal-tar, produced in the manufacture of coal-gas. The freezing-point of acetic acid is 17°; that of benzene is 4.9°. It was found in 1884 by **Raoult**, Professor of Chemistry in Grenoble in the South of France, that while 1.52 grams of camphor (the hundredth part of its molecular weight) dissolved in benzene (100 grams of solution) lowered the freezing-point of the benzene by 0.514°, the same quantity of camphor, forming a solution in acetic acid of the same strength, lowered the freezing-point of the latter by 0.39°. And he also noticed that the lowering of the freezing-point is proportional, at least in some cases, to the molecular weights of the solvents. Thus, the molecular weights of acetic acid and benzene are respectively 60 and 78; and as 0.39 : 0.514 :: 60 : 79, the proportionality is very nearly exact.

It is possible by this means to determine the molecular weight of any substance which will dissolve in any solvent for which the depression produced in the freezing-point is known. Thus, for example, **Beckmann**, the deviser of the apparatus with which such determinations are made, found that a solution of naphthalene, a white compound of carbon and hydrogen contained in coal-tar, in acetic acid, the solution containing 0.452 per cent. of naphthalene, lowered the freezing-point of acetic acid by 0.140°. A 1 per cent. solution would therefore cause a lowering of 0.309°. And as 0.31 : 0.39 :: 100 : 126, this is therefore the molecular weight of naphthalene. The simplest formula for naphthalene is C_5H_4, for its percentage composition is carbon, 93.75, hydrogen, 6.25; and to find the relative number of atoms, the percentage of carbon must be divided by the *atomic weight* of carbon, and that of hydrogen by its atomic *weight, thus:*—$\frac{93.75}{12} = 7.81$, and $\frac{6.25}{1} = 6.25$; and these

numbers are to each other in the proportion 5 : 4. But a substance with the formula C_5H_4 must have the molecular weight $(5 \times 12) + (4 \times 1) = 64$; whereas the molecular weight found is 126. Now, 126 is nearly twice 64; hence the formula of naphthalene must be $C_{10}H_8$. The method is not exact, but it affords evidence which, taken in conjunction with the analysis of the compound, enables the molecular weight to be determined.

Measurement of Osmotic Pressure by Rise of Boiling-point.—A method for determining the molecular weights of substances by the rise of boiling-point of their solutions was also devised by Beckmann, and it is frequently used. The process is analogous to that in which the depression of freezing-point is made use of. Every pure substance has a perfectly definite boiling-point, provided that pressure is constant; but if any substance is dissolved in a pure liquid, the boiling-point of the latter is raised; and it is found that the rise of boiling-point is proportional to the number of molecules of the dissolved substance present. As an example, let us calculate the molecular weight of iodine dissolved in ether from the rise in the boiling-point of the ether. The rise caused by the hundredth part of the molecular weight of a substance taken in grams, and dissolved in 100 grams of ether, is 0.2105°. Now, Beckmann found that 1.513 grams of iodine dissolved in 100 grams of ether raised the boiling-point of the ether by 0.126°. And to raise the boiling-point by 0.2105°, 2.53 grams of iodine would have been necessary; 2.53 is therefore the hundredth part of the molecular weight of iodine. It is possible to weigh iodine in the state of gas, for it is an easily volatilised element; and its vapour has been found to be 126 times as heavy as hydrogen. We have seen that this statement implies that a molecule of iodine gas is 126 times as heavy as a molecule of hydrogen gas; and as a molecule of hydrogen consists *of two atoms*, a molecule of iodine gas is 252 times as *heavy as* an atom of hydrogen, or its molecular weight.

is 252. The number obtained from the density of the gas is accordingly almost identical with that obtained from the rise in the boiling-point of ether.

We have now studied four methods by means of which the molecular weights of elements and compounds have been ascertained; they are:—

(1) By determining the density of the substance in the state of gas with reference to hydrogen, and doubling the number obtained; for molecular weights are referred to the weight of an atom of hydrogen, while a molecule, it is believed, consists of two atoms.

(2) By measuring the osmotic pressure exerted by a solution of the substance, and comparing the pressure with that exerted by an equal number of molecules of hydrogen, occupying the same volume, at the same temperature.

(3) By comparing the depression in freezing-point of a solvent containing the substance in solution, with the depression produced by the hundredth part of the molecular weight in grams of a substance of which the molecular weight is known, and by then making use of the known fact that equal numbers of molecules produce equal depression in the freezing-point of a solvent.

(4) By a similar method applied to the rise in boiling-point of a solvent caused by the presence of a known weight of the substance of which the molecular weight is required.

CHAPTER III

Dissociation—Electrolytic Dissociation or Ionisation.

Dissociation.—A certain number of substances are known which apparently do not conform to the laws which have been explained in the last chapter. For example, the compound of ammonia with hydrochloric acid, which has the formula NH_4Cl, should have the density 26.75, for the atomic weights of the elements it contains are $N = 14$; $H = 1$; $Cl = 35.5$; and the molecular weight is the sum of $14 + 4 + 35.5 = 53.5$. But the found density is only one quarter of this number, viz., 13.375. It was at first imagined that this discrepancy was to be explained by abnormal expansion of the gas; but with such a supposition, of course, Avogadro's law could not hold. Other substances which show the same "abnormal densities" are pentachloride of phosphorus and sulphuric acid. To explain this abnormality, **Henri Saint-Claire Deville** propounded the idea that such substances do not go into the state of gas as compounds, but that they split into simpler components, each of which has its usual density, and a mixture of the components will exhibit a mean density. Thus, if ammonium chloride be imagined to decompose into ammonia and hydrogen chloride on changing into gas, then the density of the supposed ammonium chloride gas will be the mean of the densities of its two constituents. Ammonia has the formula NH_3, and hydrogen chloride, HCl; the former has the density 8.5, and the latter, 18.25; and the

mean of these two numbers is 13.375. Phosphoric chloride, which has the formula PCl_5, splits in a similar manner into PCl_3 and Cl_2; and sulphuric acid, H_2SO_4, into water, H_2O, and sulphuric anhydride, SO_3. To this kind of decomposition, where the bodies which are decomposed by a rise of temperature re-unite on cooling to form the original substance, Deville gave the name **dissociation.** It has been found possible, by taking advantage of the fact that light gases, like ammonia, pass out through an opening, or, as it is termed, "diffuse" more rapidly than heavier gases, like hydrogen chloride, to separate these gases, and thus to prove that they exist as such in the vapour of ammonium chloride; for compounds are not decomposed into their constituents by diffusion; hydrogen chloride diffuses as such, and is not split into hydrogen and chlorine.

Let us look at this dissociation from another standpoint. We know that if 2 grams of hydrogen, or 32 grams of oxygen, or 28 grams of nitrogen, or, in fact, the molecular weight of any gas expressed in grams, be caused to occupy 22,380 cubic centimeters at 0° C., the pressure exerted by the gas will be 76 centimeters of mercury. If the temperature is higher, the pressure will be increased proportionally to the increase in absolute temperature. Thus, suppose the temperature were 300° C., the pressure would be increased in the proportion 273° Abs. : 573° Abs. :: 76cms. : 160cms. Now, if 53.5 grams of ammonium chloride were placed in a vacuous vessel of 22,380 cc. capacity, and the temperature were raised to 300° C., and if no dissociation were to take place, one would expect a pressure equal to that of 160 cms. of mercury. It has been found, however, that the actual pressure is twice that amount, or 320 cms. In order to account for the doubled pressure, the supposition that dissociation has taken place must again be made; that *is, in order that the* pressure must be doubled, twice as many *molecules must be* present as one would have supposed from *the weight taken.* The fact of dissociation may accordingl

be inferred either from a diminished density or from an increased pressure.

"Dissociation" of Salts in Solution.—Few measurements of the osmotic pressure of salts have been made, owing to the difficulty in producing a membrane which shall allow water to pass, and which shall be impermeable to salts. But very numerous measurements of the depression in freezing-point and the rise in boiling-point of solutions of salts have been made; and it has been already explained that these quantities are proportional to the osmotic pressure of the dissolved substances. It has been experimentally discovered that in all such cases the fall in freezing-point, or the rise in boiling-point is too great for the supposed molecular weight of the salt. It must be concluded that the osmotic pressure would also be increased, were it possible to measure it. But the fall in freezing-point or the rise in boiling-point does not imply a doubled osmotic pressure, when there is reason to expect it, unless the solution is very dilute. Now, if the pressure were doubled, we might argue from such cases as ammonium chloride that dissociation into two portions had occurred; but in moderately concentrated solutions, as the pressure is not doubled, it must be concluded that the dissociation is not complete; it is only in very dilute solutions that complete dissociation can be imagined to have taken place. Cases are known where substances in the state of gas undergo gradual dissociation, and then the pressure does not attain its maximum until the temperature has been sufficiently raised or the pressure sufficiently reduced. The reason that this is not noticed with ammonium chloride is that the temperature of complete dissociation has been reached before the substance turns to gas.

Common salt is chloride of sodium; its formula is NaCl; and for long the suggestion that it dissociated into an atom of sodium and an atom of chlorine on being dissolved in water was received as too improbable to be worth consideration. There is, of course, another way out of the difficulty; it is to suppose that a molecule of

salt has the formula Na_2Cl_2, and that the atomic weights of sodium and chlorine are respectively 11.5 and 17.75—a supposition which is contrary to other reasoning (see pp. 14–16); in that case, 58.5 grams of salt—$(2 \times 11.5) + (2 \times 17.75)$—dissolved in 10,000 grams of water should produce the normal lowering of freezing-point; or, if it produced a larger lowering, it might be supposed that these complex molecules had split more or less completely into the simpler molecules, NaCl. But though the explanation suggested might account for this instance, it is incapable of accounting for the fact that chloride of barium, which is known to possess the formula $BaCl_2$ (or a multiple thereof), gives, in sufficiently dilute solution, a depression three times that which one would have expected from its supposed molecular weight, or that ferricyanide of potassium and ferrocyanide of potassium, the formulæ of which are respectively $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$, should give four and five times the expected depression. But these results are quite consistent with the hypothesis that

$NaCl + Aq$ decomposes into Na.Aq and Cl.Aq;

$BaCl_2 + Aq$ decomposes into Ba.Aq and Cl.Aq, and Cl.Aq;

$K_3Fe(CN)_6 + Aq$ decomposes into K.Aq + K.Aq + K.Aq, and $Fe(CN)_6$.Aq; and

$K_4Fe(CN)_6 + Aq$ decomposes into K.Aq + K.Aq + K.Aq + K.Aq, and $Fe(CN)_6$.Aq.

(The symbol "Aq" stands for an indefinite but large amount of water—"aqua.") Here again we are face to face with facts and an attempted explanation. The facts are that certain compounds, which have long been known as "salts," give too great a depression of the freezing-point or too great a rise of boiling-point of the solvent in which they are dissolved, corresponding to too great an osmotic pressure. It has been observed that when the dilution is sufficient the depression in each case reaches a maximum, and that that maximum is two, three, four, or five times what might be expected; and in each case it is possible to divide the salt into two, three, four, or five imaginary portions, which often consist of atoms, though frequently of groups of atoms.

Electrolytic Conductivity of Salt Solutions.—This hypothesis, that a kind of dissociation takes place in salt solution, might have failed to gain acceptance had it not been for a very remarkable coincidence. It appears that all solutions which show this behaviour allow an electric current to pass through them, whereas all solutions of compounds such as cane-sugar, do not permit the passage of a current of electricity. The latter class of compounds is called "non-conducting;" the former class contains compounds which are "conductors" of electricity. But metals and certain compounds, chiefly consisting of the sulphides of the metals, are also conductors of electricity, with this difference, however: while the latter are apparently unaltered by the passage of the electric current, solutions of salts undergo profound change. In some cases, oxygen appears in bubbles at the plate connected with the positive pole of the battery, while hydrogen is evolved from that connected with the negative pole; in others, when the dissolved substance is a salt of such metals as copper, silver, or mercury, the metals themselves are deposited on the negative pole, or, as it is usually termed, the "kathode;" while if chlorine, bromine, or iodine is one of the constituents of the salt, it is evolved at the "anode" or positive pole.

Faraday's Law.—It was discovered in 1833 by **Michael Faraday**, Professor of Chemistry in the Royal Institution in London, that if an electric current be passed simultaneously through different solutions, the weights of metals deposited or of elements or groups of elements liberated are proportional to their equivalents (see p. 15). If the same current be passed, for example, through a solution of dilute sulphuric acid, copper sulphate, and iodide of potassium, each contained in its own vessel, provided with plates of platinum or some other unattackable metal dipping into the solution, for every gram of hydrogen evolved from the kathode in the vessel containing sulphuric acid, 8 grams of oxygen are *evolved from* the anode; 31.8 grams of copper are *deposited on* the kathode dipping into the copper solution

while 8 grams of oxygen rise in bubbles from the anode; and lastly, 127 grams of iodine are liberated from the anode in the vessel containing potassium iodide, 1 gram of hydrogen rising from the kathode. The evolution of hydrogen instead of the deposition of potassium is due to the fact that the metal potassium is unable to exist in presence of water, but immediately displaces its equivalent of hydrogen. All these numbers are in the proportions of the equivalents of the elements. And without the liberation of these elements no current passes. The elements may, therefore, in a certain sense, be said to convey the electricity; and as the same quantity of electricity passes through each solution, liberating equivalents of the elements in each case, it would appear that the same quantity of electricity is conveyed by quantities of elements proportional to their equivalents. The equivalent of an element, it will be remembered, is the weight of the element which can combine with or replace one part by weight of hydrogen; it may be identical with, or it may be a fraction of the atomic weight. In the instances given above, the equivalents of iodine and of potassium are identical in numerical value with their atomic weights; but those of oxygen and of copper, 8 and 31.8, are half their atomic weights, which are respectively 16 and 63.6. It would follow, therefore, that an atom of copper or of oxygen is capable of conveying a quantity of electricity twice as great as that conveyed by an atom of hydrogen or of iodine.

But how is it known that the atoms "convey" quantities of electricity? Must they be imagined as like boats, taking in their load of electricity at one pole, and ferrying it over to the other, and there discharging? It was at one time held that the process rather resembled the method of loading a barge with bricks, where a row of men, who may stand for the atoms, pass bricks, representing the electricity, from one to the other. But it was proved by **Hittorf** that the charged atoms actually travel or "migrate" from one pole to the other, carrying with

them their electric charges. And the charged atoms, for which the name "ions," or "things which go," was devised by Faraday, do not always move at the same rates. The rate of motion depends on the friction which the ions undergo on moving through the water or other solvent in which the salt is dissolved. This friction is different for different ions; it also depends on the particular solvent employed; and it is diminished if the temperature is raised. The force which impels the ions is the same as that commonly known as electric attraction and repulsion; the negatively charged atoms or "kations" being repelled from the negative and attracted by the positive electrode dipping into the solution, while the positively charged atoms or "anions" are repelled by the anode and attracted by the kathode.

When the anions touch the kathode, they are discharged; and similarly, when the kations touch the anode, they lose their charge. And for every anion discharged, a kation must simultaneously lose its charge. The result of this is that the number of anions remaining in solution must always be equivalent to the number of kations. It need not always be the same, for it is possible for a kation like copper to carry twice the charge (although of a different sign) of an anion like chlorine; but the number of electric charges must always be the same, although some ions are capable of carrying more than one unit of charge. There can never, therefore, be an excess of, say, copper ions in solution; for they are always balanced by the requisite number of anions. Thus, if the solution be evaporated, the remaining salt has its usual composition; though, of course, there is less of it than if none had been decomposed.

Hittorf's Migration Constants.—The fact that ions move at different rates can be demonstrated in two ways, one direct, the other indirect. The indirect method was devised by Hittorf; the direct method, which is much more recent, was first suggested by **Lodge**.

It is always advisable to form a mental picture, if possible, of any physical phenomenon, pour préciser les

idées, as the French say; and a trivial illustration will be now given which may render Hittorf's conception clearer. Imagine a ball-room with a door at each end. Suppose the partners to be all separated from each other; and suppose an order to be given that the men shall march to one door at twice the rate at which the ladies make for the other door; but that at the same time, for every man who passes through the one door, only one lady shall pass through the other door. At a given signal, say when half the ballroom has escaped, let the condition of the room be examined. It is easy to see that there will be an equal number of men and women in the room, but that there will be a greater number round the door at which the men issue than round that at which the ladies are trying to escape. And the rates of motion will be proportional to the relative numbers in each half of the ballroom, for the greater the rates at which the men move proportionally to the ladies, the greater will be the number in that part of the room at which the men are escaping.

This is a conception in close analogy with Hittorf's. The men and women are the anions and kations; and on analysing the solutions round the anode and kathode, he found that the concentration was, as a rule, altered, so that he was forced to conclude that the rate of motion towards the pole at which the concentration was increased was more rapid than that towards the pole at which he found the concentration to be diminished. By comparing the concentrations, too, he calculated the relative rates of motion of the anions and the kations towards the kathode and the anode respectively.

Lodge's direct method has recently been improved by **Orme Masson**, and very accurate results have been obtained by him. His plan is to trace the rate of motion of the anions by following them up with a coloured anion, *such as the copper* ion, which is blue, and can be seen, *while the rate of* motion of the kation is indicated by *following it up with* a coloured kation: the one he used

for this purpose is the chromate ion, which is orange-yellow. The apparatus which Masson employed consisted of two flasks connected together by a narrow tube. This tube is filled with a solution of the salt of which the rate of migration of the ions is to be determined, but in order to prevent diffusion of the liquid, or escape owing to currents produced by differences of temperature, the water in which the salt is dissolved contains enough gelatine to make it set into a jelly when cold. It is found that the gelatine does not appreciably interfere with the motion of the ions. The one flask was charged with a solution of copper chloride, and the anode plate was of copper. The other flask was charged with a dilute solution of a mixture of chromate and bichromate of potassium, and the kathode was of platinum. The connecting tube was filled with a warm solution of the salt to be examined, say potassium chloride, in water containing gelatine, and after it had cooled and set it was placed in position. On passing the current, the potassions migrate towards the kathode, and are followed closely by the blue cuprions, which serve to mark the position of the rearmost of the potassions. The chlorions, on the other hand, migrate towards the anode, followed by the orange-yellow chromations, which reveal their position. The rates can be measured by following the advance of the colour in the tubes. If the ions have equal velocity, as is nearly the case with potassions and chlorions, the meeting-place of the blue and the orange is nearly at the middle of the tube; but if, as in most other cases, the rates are different, the point of junction will be at one side or other of the middle point of the tube. The distances traversed in the same time give a direct measure of the relative velocities of the anion and kation. Having established this ratio, another salt, say sodium chloride, having a different anion but the same kation, can be employed, and so the relative rates of potassion and sodion may be compared.

The table which follows gives the rates of migration of

a few ions compared with that of potassion, which is taken as 100.

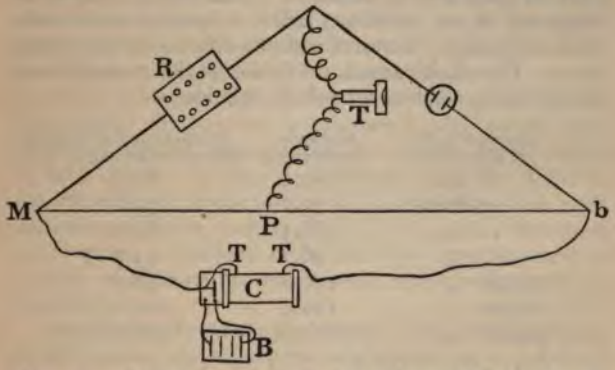
K	Na	Li	NH_4	Mg/2	Cl	$SO_4/2$
100	65.6	45.0	100	40.5	97.0	87.7

As the conductivity for a current depends on the velocity both of the anion and the kation, relative numbers for the conductivity may be obtained for any salt by adding the numbers of the individual ions given above. Thus, if it is required to find the conductivity of lithium sulphate, which has the formula Li_2SO_4, we have $Li = 45$, and $\frac{SO_4}{2} = 87.7$, together equal to 132.7.

Measurement of the Extent of Ionisation.—It is found in practice, however, that the conductivity of salts agrees with the numbers deduced from the velocity of their ions only when the solution is a very dilute one, and even then not always. This can be ascribed to either or to both of two causes. If the solution is a strong one, the molecules of salt may bear an appreciable ratio to the molecules of water, and may interfere by their possibly greater friction with the free transit of the ions. Or, on the other hand, some of the molecules may not be resolved into ions, and there may be fewer "boats" to carry across the electric charges, the progress of which towards the anode and the kathode must consequently be slower, for the non-ionised molecules take no share in the conveyance of electricity. And as the conveyance of electricity depends on the number of ions and on the rate at which they move, if the latter is known, the relative number of ions may be calculated from measurements of the conductivity of the solution.

Conductivity of Electrolytes.—To measure the **conductivity** of a solution, a "gram-molecular-weight," *i.e.* the molecular weight of the salt taken in grams, is *dissolved in a* litre of water. A small quantity of this *solution is placed in* a small beaker immersed in a large *tank of water, so* that the temperature may not vary; for

the conductivity increases with rise of temperature, owing to the smaller resistance offered by hot water to the passage of the ions, than by cold. Two circular platinum plates, the surfaces of which have been roughened by having platinum deposited on them, are immersed in the solution, so that one lies at the bottom of the beaker, while the other is one centimeter distant from it, higher up in the liquid. The wire connected with the lower plate is protected by a glass tube, in order that the current may pass only between the plates. To measure the conductivity of this solution an arrangement termed a "Wheatstone's bridge" is employed,



the construction of which will be understood from the annexed diagram. B is a battery, actuating a small toy coil, C, from the secondary terminals of which T T wires proceed to the measuring-bridge Mb, which consists of a straight piece of nickel-silver wire stretched along a scale. From one end of the bridge, *b*, the current traverses the solution; towards the other, M, the current passes through a resistance-box, R, containing bobbins of wire of known resistance, the number and resistance of which can be varied at will until the resistance is nearly equal to that of the solution. *If they are* exactly equal, and if the pointer P is exactly in

the middle of the bridge-wire Mb, then no sound can be heard in the telephone T. The resistance of the solution can then be read from the box. If, as generally happens, the resistance of the solution is not equal to that in the box, it is necessary to move the pointer P until the resistances are equal. Having thus ascertained the resistance of the solution, a portion is diluted with water, so that its strength is exactly half of the former, and the resistance is again determined. Successive dilutions in which the volume of the solution is doubled, and again doubled, are made, and in this manner the resistance due to an equal number of molecules in each case is calculated. The conductivity is the reciprocal of the resistance, and it is found that the molecular conductivity increases with the dilution up to a certain point. Thus **Kohlrausch**, the deviser of this method, found the following numbers for sodium chloride :—

Concentration : 58.5 grams in	Molecular conductivity.	Relative number of ions per 100 molecules of salt.
1 litre	69.5	67.5
2 litres	75.7	73.6
10 ,,	86.5	84.1
100 ,,	96.2	93.5
1,000 ,,	100.8	98.0
10,000 ,,	102.9	100.0
50,000 ,,	102.8	100.0

It is evident that 58.5 grams of salt dissolved in 10,000 litres of water give a maximum conductivity, for the dilution to 50,000 litres is attended by no further increase. That the altered velocity is not influenced by the frictional resistance of the water is obvious, for the solution of 58.5 grams of salt in 10 litres of water does not differ much from pure water in this respect. The increase in conductivity must accordingly be attributed to an increase in the *number of ions* at the expense of the molecules ; and, as *a dilution in* 50,000 litres of water produces no greater *conductivity* than in 10,000, it must be concluded that

complete ionisation has taken place. The figures in the last column are obtained by simple proportion, thus :—As 102.9 : 69.5 :: 100 : 67.5.

The extent of ionisation calculated from the conductivities of salt solutions agrees well in the main with that calculated from the depressions of freezing-point.

Conductivity of Pure Water.—Two points remain to be mentioned. One has reference to the conductivity of pure water. It is no easy matter to prepare pure water; even after the water has been distilled, it contains traces of substances which are ionised, such as carbonic acid or ammonia. It is possible, by employing special precautions, to add to the water before distillation substances which form non-volatile compounds with these impurities, and by making use of vessels of gold or platinum, which are not attacked, however slightly, by water, to produce almost pure water. Such water is not wholly devoid of conductivity, but its resistance to the passage of electricity is very great. It must be presumed that the water is for the most part molecules of H_2O, or perhaps even more complex molecules, such as H_4O_2, H_6O_3, &c. But there are, besides, a few ions of H and OH; so that water is capable of reacting in certain cases where ions might be suspected.

Conductivity of Fused Salts.—Another fact which is well known, and largely put to practical use, is that fused salts are, as a rule, good electrolytic conductors of electricity. Even when the salt is as pure as it can be made, it still conducts in the molten state. Although the conductivity of fused salts has not been investigated with the same completeness as that of solutions, yet it cannot be doubted that the salt must be more or less ionised. The ionisation appears to increase with rise of temperature, for the salt becomes a better conductor. This, however, may be due, in part at least, to the smaller frictional resistance which it offers to the passage of the ions towards the electrodes. But recent experiments have shown that the molecules of

some salts, at least—those in which measurement is possible—are more complex than would be supposed from their formulæ. Thus, nitre, KNO_3, consists of molecules of four times that complexity, or $K_4N_4O_{12}$; and it is not improbable that among these complex molecules there are some ions of K and of NO_3 capable of conveying an electric charge. It may indeed be stated that those liquids which possess complex molecules have the power of ionising salts dissolved in them. Water is one of the most striking examples; and it is to be presumed that such complex molecules are able to surround and prevent ions from at once discharging into one another by protecting them from each other.

The Nature of Electricity.—It has until recently been the custom to avoid speculation regarding the true nature of electricity, and to represent its presence or absence by the positive sign + and the negative sign −. Later, the existence of two kinds of electricity was thought more probable, and they were designated positive and negative electricity, the idea of a surplus or of a deficit being tacitly abandoned.

In 1881, it was pointed out by **Helmholtz**, Professor of Physics in Berlin, in a lecture delivered before the Chemical Society, that electricity behaves as if it were two "substances, which cannot be generated or destroyed, but which can be neutralised and rendered imperceptible by their union." And he went on to say that "the most startling effect of Faraday's law is this . . . that we cannot avoid concluding that electricity also, positive as well as negative, is divided into definite elementary portions, which behave like atoms of electricity."

It has come to be recognised as probable, chiefly by the labours of Professor **J. J. Thomson** of Cambridge, that the "substance" mentioned by Helmholtz is what has *hitherto been* called "negative" electricity, and that what *has been known* as "positive" electricity is the absence *of that substance*. Indeed it would appear as if a theory,

closely resembling that of phlogiston, had persisted almost until the present day. For "phlogiston" came to mean "absence of oxygen," just as "positive electricity" should bear the meaning "absence of electricity." And further, it has been shown to be likely that just as matter consists of atoms, so electricity consists of particles, which, however, are not named atoms, but in accordance with a suggestion of Dr. **Johnstone Stoney**, *electrons*. An electron, then, may be defined as a particle or corpuscle (literally, *little body*) of "negative" electricity.

In a solution of a salt such as common salt, or sodium chloride, NaCl, the ions, as has been shown, are charged atoms of sodium and of chlorine; the sodium carrying a "positive" and the chlorine a "negative" charge. From the modern point of view, it must be concluded that the chlorine ion is in reality complex; it consists of an atom of chlorine, Cl, in union with an electron, which may receive the symbol E. It may therefore be represented as ClE. The sodium ion, or "sodion," as it is sometimes called, would then be symbolised as an atom of an element Na, unburdened with an electron.

Now common salt can be made by heating the metal sodium, and plunging it while hot into a jar of chlorine gas. The act of union, which is accompanied by the evolution of much heat, may be conceived to take place with transference of an electron from the metallic sodium into such a position that it serves to bind together the Na and the Cl.

The electron originally attached to the sodium, ENa, then forms a bond, or connecting link between Na and Cl, thus, NaECl, and the product is solid white salt. On dissolving in water, the Na parts company for the most part from the ClE (see p. 42), and the two ions Na and ClE now exist side by side in the liquid.

Electrolysis.—It is possible, by various means, to withdraw electrons from, and also to add electrons to any object. One of the best known means of accomplishing this is a

galvanic battery or cell (see below, p. 47). Suppose that two platinum plates or electrodes are dipped in a solution of sodium chloride, and that one of the plates is connected with the "positive," and the other with the "negative" pole of a battery by means of wires. Electrons will be withdrawn from the liquid at the former, and forced into the liquid at the latter, pole. In fact, a battery may be regarded as a combined force-pump or suction-pump for electrons.

The primary products are ENa, or metallic sodium, and Cl; for the Na ions, being attracted by the electrons at the surface of the electrode, move towards the plate, touch it, and each receives an electron. Similarly, the removal of electrons from the "positive" pole causes the chlorine ions, ClE, to wander towards that pole; and when they touch it, an electron leaves each chlorine ion, and elementary chlorine is set free.

The sodium, however, immediately on liberation, transfers its electron to the hydrogen of water. While by far the larger number of water molecules exist in a non-ionised state, as H_2E_2O, a few are present as H and EOEH, *i.e.* as ions of hydrogen, and ions of hydroxyl. Each ion of hydrogen receives an electron from each atom of sodium as it touches the "negative" electrode; and every two atoms of hydrogen combine, forming HEHE, one electron serving to bind together the atoms into molecular hydrogen.

Let us now follow the discharged chlorine ions, which have each lost an electron. Here, too, the element is liberated, for the most part. It would lead us too far to follow subsidiary reactions; let us suppose that free chlorine is the only product. Now, there is reason to believe that elementary chlorine is, like other elements, a compound of electrons with an underlying substance; reasons which will be discussed later in the book. And it is probable that with each atom, seven electrons are associated. But most of these *are "latent"; i.e.* there is little tendency for the atom of *chlorine to part* with them. However, when two atoms of *chlorine are set free*, by having parted with the two electrons

transferred to them by the hydrogen during the act of ionisation, one or more (we will here suppose one) of the latent electrons of each atom comes into play, and the two atoms combine, forming a molecule, the symbol of which would be $E_6ClECIE_7$; the external E's representing latent electrons, which do not manifest themselves during this change.

The notation employed will have been partly grasped by this instance; but it may tend towards a better understanding if the somewhat fuller explanation given on p. 61 is referred to.

The Galvanic Battery.—Different metals tend to give off electrons, but not all with the same rapidity; those which are termed more "electro-positive," such as magnesium or zinc, part with electrons more readily than copper or silver, which are classed as more "electro-negative." In fact E_2Zn is a more easily dissociated substance than E_2Cu. Hence, as electrons can pass easily through and along metallic wires, if a zinc plate and a copper plate, connected externally by a wire, be dipped in a solution of hydrogen chloride, hydrogen will be liberated at the copper plate, and an electric current will pass along the wire. It is to be supposed that metallic zinc, E_2Zn, becomes ionised; that is, it loses its electrons, which find their way up the plate, and along the wire to the copper plate; while for every two electrons which thus change their place, an ion of zinc, Zn, enters the liquid. It is true that copper, E_2Cu, has also a tendency to part with its electrons; but inasmuch as the flow is from zinc plate to copper plate, the copper gains, and does not lose, electrons. On arriving at the surface of the copper, these electrons are met by hydrogen ions, H, ready to combine each with an electron to form EH; after combination, the molecule HEHE is formed, which constitutes gaseous hydrogen, escaping in bubbles. In the liquid, therefore, hydrogen ions continually migrate to the copper plate in order to receive electrons; while *chlorine ions*, ClE, find their way towards the zinc plate with *a less velocity*. A current of electrons consequently passes

continuously through the wire from the zinc to the copper plate. If the cause of this flow of electrons be inquired into, several suggestions may be made. It might, for example, be supposed that the hydrogen ions attract electrons out of the copper; no doubt this is true; but if this were the only cause then the electric pressure, or "potential," would be the same, if other metals were substituted for the zinc or for the copper. But that is not the case; if a tin plate be substituted for a zinc one, the "potential" is not so great, and the number of electrons passing along the wire will be less, other things being equal. Hence it is reasonable to suppose that the flow is caused by the different rates at which copper and zinc part with their electrons.

It may also be remarked that the passage of the current presents some analogy with the flow of water through a semi-permeable membrane in causing osmotic pressure (see p. 24); it will be remembered that such a membrane is impermeable to the passage of sugar-molecules, while it permits water-molecules to pass. Now a copper wire is permeable to electrons, although it is impervious to atoms; hence the electrons pass through the wire, rather than through the liquid electrolyte.

To sum up:—Certain substances, in the state of gas, exhibit dissociation—that is, they decompose into simpler constituents, which combine again on cooling. This dissociation is favoured by a rise of temperature or by a lowered pressure, and reversed by a fall of temperature or a rise of pressure. From a determination of the density of the mixture of gases the extent of the dissociation can be calculated. Certain substances, in like manner, and such substances are generally named "salts," when dissolved in water or certain other solvents, undergo electric dissociation or ionisation; this dissociation is often increased by a rise of temperature, and always by dilution. The constituents of such solutions, *the anions and kations*, can be urged in opposite directions *by an electric current*; they usually "migrate" at different *rates*; and when they discharge, by contact with the elec-

trodes, they are sometimes liberated in the free state, as, for example, many metals, and bromine and iodine; but sometimes the discharged ions are incapable of existing in the free state in contact with the solvent, and in this case they react with the water, and form new secondary compounds. The amount of this ionisation can be measured by determinations of the depression of freezing-point, or of the conductivity, of the solution.

Electricity is a substance; its intimate particles are termed "electrons." Metals are compounds of electrons with forms of matter known as metallic ions; chemical combination consists in a transfer of one or more electrons to the compound, the electron forming a bond between the atoms. When dissolved, such compounds generally undergo dissociation, and the ions are freed from each other; and they can then be freed as elements by the addition of electrons to metallic ions, and by the removal of electrons from non-metallic ions. A battery is a machine whereby electrons can be removed from, or added to, ions; a sort of electric force-pump and suction-pump.

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CHAPTER IV

Elements:—Methods of Preparation; Classification; Valency. Compounds:—Structural Formulæ; Classification; Nomenclature.

We have seen, in Chapter I., how the idea of an "element" as a constituent of compounds gradually became more defined. As fresh discoveries were made, it was found that certain substances could not further be decomposed, yielding new constituents. But it is not easy always to determine whether or no a substance is an element. For certain compounds are very stable, that is, are very difficult to decompose; and it has happened several times that such compounds were mistaken for elements. A remarkable instance is a copper-coloured body, found in the débris left in the hearth of an old iron furnace, which was for long supposed to be the element titanium; more careful investigation, however, proved it to be a compound of titanium with nitrogen and carbon.

Methods of Preparing Elements.—There are three methods by which elements have been prepared, and all elements have been made by one of these methods. They are:—

(1) **Separation of the Element by Means of an Electric Current.**—We have already seen that the compound must be ionised, and this is attained only after dissolving it in water or some other appropriate solvent, or after fusing it. It is the act of solution or of fusion which separates the ions; and the effect of the current is to

add electrons to the "positive," and to remove them from the "negative" ions; they then assume the form of the free elements. It is necessary, in order that this method shall succeed, that the discharged ion shall not act on the solvent, nor on the electrode. It is impossible, for instance, to deposit sodium from an aqueous solution of any of its salts, for no sooner has the sodium received an electron than it is attacked by the water; hydrogen is evolved in equivalent amount to the sodium, and sodium hydroxide is produced, in which the sodium has taken the place of one of the hydrogen atoms in water; its formula is therefore NaOH. Chlorine, too, cannot be produced by the electrolysis of a chloride, if the anode is of iron, for example, for ions of iron enter the solution, instead of chlorine coming off as an element.

(2) **Separation of an Element from a Compound by Heat.**—There appears to be little doubt that at a sufficiently high temperature all compounds would be decomposed into their elements: in the sun, which possesses a temperature much higher than can be reached by any means at our disposal, it is probable that all compounds are decomposed. But certain compounds, like silica or quartz, for example, are so stable that they resist the highest temperature which we can give them, without any change, except fusion and volatilisation. There is, moreover, another reason why this process often fails to isolate an element. The compound may be decomposed on heating, but its constituents may re-unite on cooling, unless one of them is more volatile than the other, and removes itself from the sphere of action. For these reasons this process of obtaining elements is of somewhat limited application. But it forms the most convenient method of preparing oxygen; for example, if oxide of mercury be heated, it decomposes into gaseous oxygen, the boiling-point of which lies far below atmospheric temperature, $-182°$; while the mercury, which boils at 358°, although it volatilises at the temperature requisite to effect the decomposition of the

oxide, condenses in the flask or tube in which the oxide is heated. Sulphide of gold, too, can be separated into gold and sulphur on being heated; for while sulphur boils at 446°, the boiling-point of gold is probably not much below 2000°.

(3) **Separation of an Element from a Compound by Displacement.**—On heating one element with a compound of another element, it not infrequently happens that the element in combination is displaced and liberated, while the other element takes its place in the compound. This is doubtless an ionic phenomenon; one element—that in combination—being ionised, receives electrons from, or parts with electrons to, the added element, which in its turn becomes ionised. A solution of iodide of sodium, for example, contains *iodions* and *sodions*, IE and Na. On adding to it a solution of chlorine in water, in which there are certainly many non-ionised chlorine molecules, ClECl, molecular iodine, IEIE is set free, while ionised chlorine, ClE, goes into solution. The free iodine forms a brown solution, or, if much is present, a black precipitate. Again, when metallic sodium is heated with magnesium chloride to a red heat, globules of metallic magnesium are set free, while the sodium enters into combination with the chlorine. It may be supposed that on fusion the magnesium chloride contains some ions of chlorine and magnesium; the non-ionised sodium gives electrons to the ionised magnesium, and the latter metal is liberated in an non-ionised state, as E_2Mg. But it may be objected that only those magnesium ions which exist as such should exchange their charges with the sodium; that is true; but when they have done so others become ionised and undergo a similar change; for if the temperature be kept constant, the ratio between the number of the ionised atoms of magnesium and the non-ionised atoms of magnesium in the chloride must remain constant, so that when the magnesium ions are replaced by sodium ions, other molecules of magnesium chloride become ionised to keep up the balance.

The element carbon is most frequently used to displace other elements. In its case, little or nothing is known of the electrical actions; but if analogy may be taken as a guide, its action may be attributed to a similar exchange of electrons between the displaced element and the carbon. But here the carbon, as soon as it unites with the oxygen which was previously in combination with the displaced element, escapes in the form of gas, CE_2O.

An essential condition for the preparation of elements by the method of displacement is that the element which it is proposed to prepare in the free state shall not itself combine with the element which is used to displace it. Thus, chlorine cannot be used to displace either carbon or sulphur from the compound of carbon with sulphur, bisulphide of carbon, since it itself combines with both the carbon and the sulphur, yielding chloride of sulphur together with chloride of carbon. In general, however, this difficulty does not occur.

The elements which are generally used for the displacement of others from their compounds are :—

1. **Free hydrogen at a red heat** which displaces elements from their oxides or chlorides.
2. **Ions of hydrogen,** on the point of receiving electrons, or hydrogen "in the nascent state," *i.e.* hydrogen being set free from its compounds by the action of a metal; it also displaces elements from their oxides or chlorides, or, in general, from their salts.
3. **Metallic sodium,** which displaces elements from their chlorides or fluorides.
4. **Metallic magnesium,** which displaces elements from their chlorides or oxides.
5. **Metallic aluminium,** which displaces elements from their oxides.
6. **Metallic iron,** which displaces elements from their sulphides.
7. **Fluorine,** which displaces oxygen from water;

chlorine in sunlight, which acts slowly in the same way; **chlorine** displaces bromine, and **bromine**, iodine.

8. **Carbon**, which is the most generally employed agent for replacing other elements; it combines with oxygen, forming carbonic oxide or carbonic anhydride gases, and liberating the element with which the oxygen was combined.

The question of cost or of convenience often decides as to which of these methods is used. In the sequel, only the more generally used plan will be described. It must be remembered, too, that the employment of these processes does not always lead to the isolation of the element; in many cases a compound is produced, containing less of the element which it was intended to remove; and it is sometimes difficult to decide whether or not an element has really been set free. Experiments on its compounds are often required to decide the question.

Classification of Elements.—For long it had been noted that certain elements displayed a marked similarity with each other. Thus the metals sodium and potassium, discovered by **Sir Humphry Davy**, are both white, soft, easily oxidisable metals, forming soluble salts with almost all acids; these salts resemble each other in colour, in crystalline form, and in other properties. The subsequently discovered metals, lithium, rubidium, and cæsium, have also a strong resemblance to potassium and sodium. Their atomic weights also increase progressively; thus we have the series, Li = 7, Na = 23, K = 39.1, Rb = 85, and Cs = 133. Similar series had been noticed with calcium, strontium, and barium; magnesium, zinc, and cadmium; and so on. It was not until 1863 that **John Newlands** called attention to the fact that if the elements be arranged in the order of their atomic weights a curious fact becomes noticeable. It is that, omitting hydrogen, the first, the eighth, the fifteenth, and, in short, all elements may be so arranged that the "difference between the number of the lowest member of a group and that immediately above it is 7; in

other words, the eighth element starting from a given one is a kind of repetition of the first, like the eighth note of an octave in music." This idea was subsequently discovered independently and elaborated by **Lothar Meyer** and by **D. Mendeléeff**, and it has now been adopted, in spite of some difficulties, as the ground-work of classification of chemical substances.

The table may be given in the following form, although there are many ways of representing the order in which the elements lie :—

The Atomic Weights of the Elements arranged*[1] *according to the Periodic System.

	H	He	Li	Be	B	C	N	O
	1	4	7	9	11	12	14	16
	F	Ne	Na	Mg	Al	Si	P	S
	19	20	23	24	27	28	31	32
Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se
56	59	59	64	65	70	72	75	79
Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te
102	103	106	108	112	114	119	120	128
?	?	?	Sm	?	Gd	?	?	?
			150		156	162	164	172
Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	?
191	193	195	197	200	204	207	208	
viii	vii	iv	iii	ii	iii	iv	v	vi
to	to	to	to	and	and	and	to	to
ii	ii	ii	i	i	i	ii	ii	ii

[1] *It is a matter of indifference which element is placed first on the list. The most convenient form to give the diagram is that of two*

It will be noticed that the number of elements in the first two horizontal rows is not seven, but eight, and that, consequently, every ninth element, and not every eighth, presents similarity with its predecessor in the vertical columns. This is owing to the more recent discovery of the elements in the second vertical column. It will also be seen that it is possible, by folding the projecting slip to one side or other, to bring new sets of elements in the third and succeeding horizontal rows beneath the elements in the first and second. The first and second rows are termed "short periods," the others, "long periods." It appears that by so arranging the elements, analogies are brought out more striking than if such long and short periods were not adopted.

Valency.—The Roman numerals below the vertical columns refer to what is termed the "valency." An element capable of combining with or replacing one atom of hydrogen, or, in other words, of which the equivalent and atomic weight are identical (see p. 15), is termed a *monad*, or is said to be *monovalent*. Thus, 23 grams of sodium replaces 1 gram of hydrogen in water or in hydrogen chloride, to form hydroxide or chloride of sodium; and as 23 is known to be the atomic weight of sodium from determinations of its specific heat, the atomic weight of sodium is expressed by the same number as its equivalent. It is therefore a monad. The element oxygen is a *dyad* or *divalent*, because, in water, two grams of hydrogen are combined with 16 grams of oxygen; its equivalent is therefore 8. But oxygen is 16 times as heavy as hydrogen—that is, a molecule of oxygen is 16 times as heavy as a molecule of hydrogen; and as a molecule of each of these substances is believed to consist of two atoms, an atom of oxygen is 16 times as heavy as an atom of hydrogen. The atomic weight is therefore 16; but as

cylinders, on which the elements follow spiral lines, so that oxygen and fluorine, sulphur and chlorine, follow each other round the smaller cylinder, while selenium and bromine, tellurium and iodine, &c., are conspicuous round the larger cylinder. The atomic weights here given are only approximate.

the equivalent is 8, the atomic weight is twice the equivalent. Hence the name "*dyad.*" Similarly, there are *trivalent* elements, or *triads*; *tetravalent* elements, or *tetrads*; *pentavalent* elements, or *pentads*; *hexavalent* elements, or *hexads*; *heptavalent* elements, or *heptads*; and possibly one *octovalent* element, or *octad.*

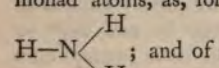
Valency of Elements.—As elements may have more than one equivalent (see p. 15), so they may have more than one valency. Certain elements, however, so far as is known, possess only one valency; examples of this are found in the lithium, the beryllium, and the boron columns. But the majority of elements exhibit more than one valency, according to circumstances. Thus, compounds of nitrogen are known possessing the formulæ NO, NH_3, NO_2, and NH_4Cl, in which one atom of nitrogen is combined with one atom of dyad oxygen, and is therefore also a dyad; with three atoms of monad hydrogen, and is accordingly a triad; with two atoms of dyad oxygen, whence nitrogen is here a tetrad; and with four atoms of monad hydrogen and one atom of monad chlorine—in all, with five monads—and in this case nitrogen must be accounted a pentad. The atomic weight of nitrogen is known from its density to be 14; and its equivalents in these compounds are respectively $\frac{14}{2}$, $\frac{14}{3}$, $\frac{14}{4}$, and $\frac{14}{5}$. This peculiarity makes the classification of some of the elements a difficult task.

But there is an additional difficulty which meets us in attempting to ascribe the valency to an element. It is connected with what is known as the "structure" of compounds. As this subject will be frequently alluded to in succeeding chapters, enough will only be said here to give an idea of the problem which faces us in attempting a rational classification of the elements.

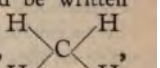
We are ignorant of the form of the atoms. It is true that various speculations have been made which may possibly lead to a true conception of their appearance and *motions*, but these are not sufficiently definite and supported by facts to require more than a passing allusion

here. For all practical purposes, we are content, in default of a better conception, to regard atoms as spheres, hard and elastic, and compounds as formed by the juxtaposition of these spheres. We suppose, too, that these atoms are associated with electrons, of the form of which we know nothing. That this conception is far from reality is more than probable, but it has to suffice. Certain deductions, however, may be drawn regarding the methods of combination of the atoms in the molecule. It is certain that molecules and electrons must occupy space of three dimensions; but just as it is possible to represent solid objects on a plane surface by the help of perspective, so it is allowable to picture molecules as made up of atoms and electrons spread over a plane surface, until we find facts which demand space of three dimensions. We shall see later that in certain cases such solid models of molecules are necessary, but, as a rule, they can be dispensed with. And instead of attempting to picture the atoms as circles or projected spheres, the symbols alone will be employed. The fact of combination will be indicated by a dash uniting the atoms; thus, a monad will have one, and only one, dash, proceeding from it; a dyad, two; a triad, three; and so on.

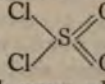
Structural Formulæ.—The simplest case which we can consider is that of a compound consisting of two monovalent atoms, such as hydrogen chloride. Here we have the structural formula, H—Cl. A compound of a dyad with two monad atoms, such as water, or its analogue, hydrogen sulphide, must have the formula, H—O—H, or H—S—H. The compound of a triad with three monad atoms, as, for example, ammonia, would be written

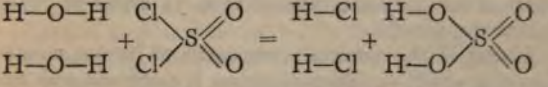


; and of a tetrad with four monads,

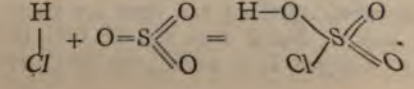


where an atom of carbon is the tetrad, and the compound is named methane, or "marsh-gas." The atom of sulphur is, however, not always divalent; it is sometimes tetravalent, as in its compounds with chlorine and with oxygen. In the first case, tetra-chloride of sulphur has the formula,

; and in the latter, sulphur dioxide is represented by the formula O=S=O. Sulphur dioxide unites directly with chlorine on exposure of a mixture of the two gases to sunlight, forming a compound named sulphuryl chloride, which has the empirical formula, SO_2Cl_2; in this compound sulphur is regarded as a hexad, hence the structural formula must be  . Now, sulphuryl chloride reacts at once with water when they are brought into contact, and sulphuric acid is produced along with hydrogen chloride. This change can be represented structurally by the equation:—



The chlorine atoms of the sulphuryl chloride have combined with two of the hydrogen atoms of two molecules of water, leaving the residues —O—H, which are termed "hydroxyl groups;" these have taken the place of the chlorine atoms, forming sulphuryl hydroxide, or, as it is commonly termed, sulphuric acid. If the foregoing representation is correct, then an intermediate substance should exist, which may be named "sulphuryl hydroxy-chloride," and which should contain a chlorine atom and a hydroxyl group, each in union with sulphuryl. Such a body has been prepared by the direct union of sulphur trioxide, where sulphur is in combination with three atoms of oxygen, with hydrogen chloride. But here there must be a transposition of the hydrogen atom, as is evident from the equation—



In a similar manner to the above schemes, the relations of the atoms in compounds may be traced out, but sometimes it is difficult to decide regarding the structure. Here is an instance. The specific heat of the element barium shows that it possesses an atomic weight not far removed from 137; the analysis of its chloride leads to the fact that 137/2 grams of barium are in combination with 35.5 grams of chlorine, and 35.5 is known to be the equivalent of chlorine; hence 63.5 is the equivalent of barium, and $63.5 \times 2 = 137$ is its atomic weight. Ordinary oxide of barium corresponds with this, for it contains 137 grams of barium in combination with 16 grams of oxygen; hence we accept barium as a dyad. But if barium oxide be heated to dull redness in a current of oxygen, another atom of oxygen combines with the oxide, and in the compound BaO_2, 137 grams of barium are combined with 32 grams of oxygen. Is barium a tetrad?

Among all the numerous compounds of barium, no one is known in which one atom of barium is combined with more than two atoms of a monad; when barium dioxide is treated with hydrochloric acid, for example, two atoms of oxygen are not replaced by four atoms of chlorine, but the change is—

$$BaO_2 + 2\,HCl = BaCl_2 + H_2O_2.$$

Hydrogen dioxide is produced. Now the formula of hydrogen dioxide has been proved by the freezing-point method to be H_2O_2, and not HO; hence it may be supposed that it consists of two hydroxyl groups in union with each other, thus: H—O—O—H; in this case, barium dioxide would be , the two atoms of oxygen being themselves united together; and there are many instances of similar union. But it may also be held that one of the atoms of oxygen is a tetrad, the other remaining a

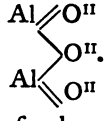
dyad, thus: ; whence barium dioxide would be Ba=O=O. Both of these views can be supported by arguments, and it is an open question which has a claim to preference. It is certain, however, that barium is not a tetrad.

In other instances, it must be confessed that the evidence is by no means so clear, and there is then considerable doubt as regards the correct classification of the elements concerned.

The electronic theory affords a satisfactory explanation of valency; and the "bonds" or "affinities," which have long been used to express valency, may be taken as abbreviations for the symbol used for electrons, E. Thus H—Cl stands for HEClE. It is true that, as we have seen on p. 46, chlorine has "latent" affinities; these are not expressed in structural formulæ, as a rule. It may be that the electronic formula for HCl should be $HEClE_7$, the E_7 being latent. In that case, when dissolved in water, the chlorine ion is $EClE_7$; and it might be symbolised as —Cl, the E_7 being disregarded as latent. We say, however, in ordinary parlance, that "both hydrogen and chlorine are monads"; that "each possesses an affinity."

The remaining formulæ on p. 58 would be written in terms of electrons, $H_8E_8NE_5$, and $H_4E_4CE_4$; SO_2 would become $E_2SE_4O_2E_4$, for sulphur is a hexad, and in this compound two electrons are latent. Sulphuryl chloride would be $\begin{matrix}E_7ClE\\E_7ClE\end{matrix} S \begin{matrix}E_2OE_2\\E_2OE_2\end{matrix}$, and sulphuric acid, $\begin{matrix}HEO(E_2)E\\HEO(E_2)E\end{matrix} S \begin{matrix}E_2OE_2\\E_2OE_2\end{matrix}$; sulphur trioxide, $E_2OE_2S(E_2OE_2)_2$.

An atom of metal may consist of an ion attached to one *or more electrons*; for example, ENa is an atom of metallic *sodium*, E_2Ba of barium, E_3Al of aluminium. These

are often expressed: Na^{I}, Ba^{II}, Al^{III}, the Roman figures signifying the valency, or the number of attached electrons. Sodium oxide may have the formula, Na_2E_2O, or if the latent electrons of oxygen be regarded, $Na_2E_2OE_2$; and again this may be written $Na_2 = O^{II}$, the Roman II representing the latent electrons. Similarly BaE_2OE_2, or $Ba = O^{II}$; and $Al_2E_6O_3E_6$, or  Aluminium oxide, indeed, when dissolved in fused cryolite, can be electrolysed; this is now the usual method of manufacturing aluminium; and in solution, the ions are $2Al$, and $3E_2OE_2$, or $2Al$ and $3 = O^{II}$.

Again, a metal need not part with all its electrons. Thus, metallic iron is probably E_3Fe; when dissolved in hydrochloric acid,

$$E_8Fe + 2H|EClE_7.\ Aq = EFe|(EClE_7)_2.\ Aq + HEHE$$

or: $$Fe^{III} + 2H|-Cl^{VII}.\ Aq = Fe^{I}|=Cl^{VII}{}_2.\ Aq + H - H^{I}.$$

On passing chlorine gas through a solution of ferrous chloride, ferric chloride is produced, thus:—

$$2EFe|E_2Cl_2E_{14}.\ Aq + E_6ClEClE_7.\ Aq = 2Fe(EClE_7)_3.\ Aq$$ or:

$$2Fe^{I} = Cl^{VII}{}_2.\ Aq + Cl^{VI} - Cl^{VII}.\ Aq = 2Fe \equiv Cl^{VII}{}_3.\ Aq$$

Ferrous chloride, in water, is largely ionised into $2Fe$, and $2EClE_7$; and ferric chloride, into Fe and $3EClE_7$.

It is not necessary, nor is it customary, to write all equations representing the transfer of electrons; but the changes which take place can readily be represented by the symbols given.

Were all the elements to be capable of combining with each other, it is easily seen that the number of compounds *would be prodigious*, and that no mind could possibly hope *to grapple with* them; but it happens that only a certain

number of elements forms well-defined compounds with the rest, and the grouping of compounds is thus not so difficult a task as might be supposed. The classes are the following:—

Classification of Compounds:—

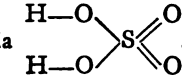
1. Hydrogen combines with a few elements, forming *hydrides*.

2. Fluorine, chlorine, bromine, and iodine combine with most elements, forming *fluorides*, *chlorides*, *bromides*, and *iodides;* this group of elements is called the *halogen* group, and their compounds are often termed *halides*.

3. Oxygen and sulphur also combine with most elements, and their compounds are named *oxides* and *sulphides*. The comparatively rare elements selenium and tellurium form similar compounds, named *selenides* and *tellurides*.

A very numerous and important class of compounds consists of those in which oxygen is combined partly with hydrogen, partly with another element. These compounds can be divided into two distinct classes, according to their behaviour in aqueous solution. Members of both classes are ionised, but they yield different ions according to the class to which they belong. An example of the first class is the compound H—O—Cl, known only in solution in water, for it decomposes when an attempt is made to free it from water. The aqueous solution is only slightly ionised, but the ions present are H and —O—Cl. The hydrogen may be displaced by metals, forming "salts," which are also ionised, and indeed much more completely than H—O—Cl. Thus we have K—O—Cl, $Ca=(O—Cl)_2$, and other similar salts, which are ionised in solution to K and —O—Cl, and to Ca and $(—O—Cl)_2$ respectively. Such hyroxides are named **acids.**

It appears, however, that elements which form this class of hydroxide are, as a rule, incapable of retaining in combination many hydroxyl groups at a time; hence compounds of this nature are generally mixed oxides and hydroxides. *It might*, for example, be imagined that triad nitrogen

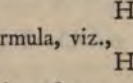
should be capable of retaining in combination three hydroxyl groups, to form H—O—N(O—H)(O—H); but the compound is unstable, and loses water, giving a mixed hydroxide and oxide, H—O—N=O. The ions in this case are H and —O—N=O. Another similar instance is that of sulphuric acid; as it contains hexad sulphur, it might be supposed that the corresponding hydroxide of sulphur would be $S(OH)_6$; but by loss of two molecules of water, sulphuric acid has the formula  , as already shown. Its ions are H, H, and $SO_4=$, or sometimes H and HSO_4—. The salts of these acids are respectively M—O—N=O and $(M—O)_2=SO_2$, where M stands for any monad metal.

Nomenclature of Compounds.—The nomenclature of this class of bodies is due to a committee of which **Lavoisier** was a member. After his discovery of the true nature of oxygen, he was led, not unnaturally, to ascribe to it the chief function in the formation of compounds, and the acids and salts were named without introducing any syllable to signify that oxygen was one of the constituents. In general, the best known or the first discovered acid was given a name terminating in "ic," such as "chloric," "sulphuric," "nitric." The salts of these acids were termed "chlorates," "sulphates," and "nitrates." The acid containing one atom of oxygen less was named with the final syllable "ous," thus: "chlorous acid," "sulphurous acid," "nitrous acid;" and the salts were termed "chlorites," "sulphites," and "nitrites." Acids containing still less oxygen were named with the prefix "hypo," thus: "*hypochlorous* acid" and "hypochlorites;" and acids and *salts containing more* oxygen than those which had names *terminating in "ic"* and "ate" were distinguished by the

prefix "per," thus: "perchloric," "persulphuric" acids, forming "perchlorates" and "persulphates." This nomenclature is still retained. It is illustrated in the table which follows:—

Hypochlorous acid, . . .	HOCl.
Chlorous acid, . . .	HOClO.
Chloric acid, . . .	$HOClO_2$.
Perchloric acid, . . .	$HOClO_3$.
Potassium hypochlorite, . .	KOCl.
„ chlorite, . .	KOClO.
„ chlorate, . .	$KOClO_2$.
„ perchlorate, . .	$KOClO_3$.

The second class of hydroxides is named "hydroxides." Members of this class, however, yield ions, one of which is always hydroxyl, —OH. As examples, we may select sodium hydroxide, Na—O—H, and calcium hydroxide, $Ca=(O—H)_2$. Here solutions of these compounds in water contain the ions Na and —OH, and $Ca=(OH)_2$. Such hydroxides are termed **bases**; but the name is also indiscriminately applied to oxides when they unite with water to form bases. Thus CuO and $Cu(OH)_2$ are each termed bases.

The same elements may sometimes form bases or acids, according to the valency. The element chromium is an instance. Chromous oxide has the formula Cr=O, corresponding to the chloride $Cr=Cl_2$; the hydroxide is analogous with the chloride, and has the formula $Cr=(OH)_2$. But there is also an oxide, CrO_3, where chromium is a hexad; the hydroxide is not known, but the acid is like sulphuric acid in formula, viz.,  . This is an instance of the rule, of very wide application, that the *character of* a compound is influenced both by the nature of

the elements contained in it, as well as by its structure and the valency of these elements.

Sulphur, and in a less degree selenium and tellurium, resemble oxygen in forming salts of nature similar to these described, as well as acids and bodies analogous to hydroxides. The nomenclature follows that of the oxides, except that the syllables "sulpho" or "thio" are interposed for the sulphur compounds. Thus we have a carbonate, K_2CO_3, and a sulpho- or thiocarbonate, K_2CS_3. In the somewhat rare cases where selenium or tellurium play a similar part, the words "selenio-" or "tellurio-" are interposed. Compounds analogous to the hydroxides are termed "hydrosulphides," "hydroselenides," or "hydrotellurides."

4. Compounds of nitrogen, phosphorus, arsenic, and antimony, with other elements, are termed *nitrides*, *phosphides*, *arsenides*, and *antimonides*. And just as double oxides of hydrogen and other elements exist, so too nitrides of hydrogen and other elements are known. The compound of nitrogen and hydrogen, ammonia, which has the formula NH_3, unites with acids, forming salts. For example, ammonium chloride, NH_4Cl, is produced by the direct union of ammonia, NH_3, with hydrogen chloride, HCl, if a trace of moisture is present. In aqueous solution it undergoes partial ionisation, and the ions are $H_4E_4NE_4$, and $EClE_7$; or H_4N^{V}, and $-Cl^{VII}$. In this it resembles sodium chloride, NaCl, and the name "ammonium" has been devised to exhibit this similarity. When ammonium chloride or similar compounds are formed by the union of ammonia with acids, it is believed that the nitrogen atom changes its valency from triad to pentad, thus:

$$H—N=H_2 \text{ and } Cl—N\begin{matrix}H_2\\ \diagup\\ \diagdown\\ H_2\end{matrix}.$$

Even in "substituted ammonias," this property of *combining with acids* is distinctive. For example, copper *bromide*, $CuBr_2$, unites directly with ammonia, giving

$Cu=(NH_2)_2 2HBr$ or $Cu=(NH_3)_2Br_2$. It will be seen that the atom of dyad copper has replaced two atoms of monad hydrogen in two molecules of ammonium bromide.

It is possible, too, for a group of elements to replace the hydrogen of ammonia, just as it is possible for a group to take the place of the hydrogen of water. Referring back to the formula of sulphuric acid, H_2SO_4, it is plain that it may be written $SO_2=(OH)_2$, and regarded as two molecules of water, in which two atoms of hydrogen have been replaced by the dyad group, SO_2. This is identical with the structural formula already given on p. 54. So, too, with nitrogen; the compound $SO_2=(NH_2)_2$ is also known, and it may be regarded as derived from two molecules of ammonia by the replacement of two atoms of hydrogen by the dyad group, SO_2".

Compounds of phosphorus, arsenic, and antimony after this pattern are not known.

5. Compounds of carbon and silicon with other elements are termed *carbides* and *silicides*. The carbides are extraordinarily numerous owing to the power possessed by carbon of forming compounds in which two or more atoms of carbon are in combination with each other. We have seen that a molecule of hydrogen consists of two atoms; a molecule of oxygen also consists of two atoms; but we know of no compounds of oxygen in which more than three atoms of oxygen are in combination with each other. With carbon, however, the case is different. Considering the combination with hydrogen alone, we have not only CH_4, but H_3C-CH_3, $H_3C-\underset{\displaystyle H\ H}{\overset{\displaystyle H\ H}{C-C}}-CH_3$, in all of which the element carbon is a tetrad, being either in combination with hydrogen or with another atom of carbon. And these compounds may have their hydrogen replaced

by other elements; for example, an atom of chlorine may take the place of an atom of hydrogen in any one of these compounds, or one or more atoms of hydrogen may be replaced by groups of hydroxyl, —OH, or two atoms of monad hydrogen may be replaced by an atom of dyad oxygen, or three atoms by one of triad nitrogen, and so on. This makes the chemistry of the carbon compounds very complicated, but at the same time it affords the means whereby the numerous constituent compounds of the tissue of plants and animals can be built up, for they consist, for the most part, of carbon compounds, containing at the same time other elements in combination with the carbon atoms. This branch of chemistry is commonly termed "Organic Chemistry," and treated separately.

6. Many elements of the metallic class, such as iron, lead, copper, sodium, &c., form compounds with each other. These compounds are usually named "alloys;" but it must be mentioned that the name "alloy" is often applied to solid mixtures of the metals where no actual compound exists.

Such are the classes into which chemical compounds may be divided. In a short sketch like the present, it is, of course, impossible to do more than consider a few of these compounds, and those will be chosen which are best adapted to illustrate the nature of the various groups. They will be considered in the second volume.

CHAPTER V

Methods of Determining the Equivalents of the Elements—Of Ascertaining their Molecular Weights—Allotropy.

The meaning of the word "equivalent" has already been explained on p. 15, and we shall now consider how the equivalent of an element may be determined. As already stated, some compound of the element is analysed, preferably one with hydrogen, oxygen, or chlorine, and the weight of the element which is in combination with, or which replaces 8 parts by weight of oxygen, is termed the equivalent of the element. But it is seldom that a direct method of estimating the equivalent can be practised, for it is not always possible to obtain a compound of the element with hydrogen, or to deprive its oxide of oxygen, or its chloride of chlorine. In fact, each element has to be specially studied, and a method devised which will lead to the required information. It is, above all, necessary that the compounds dealt with shall be pure—that is, that they shall not contain any other elements than those which it is desired to estimate, and that their composition shall be definite. For instance, if it were desired to find the equivalent of barium by estimating the proportion of chlorine in its chloride, it would be essential to obtain barium chloride free from the very similar elements calcium and strontium, and it would also be of the first importance to make sure that in weighing the chloride, the specimen should be free *from water* adhering to the powdered substance.

Methods of Determining the Equivalents of Elements.—It is not always necessary to determine both constituents of the compound; for example, the ratio of silver to chlorine can be found by dissolving a known weight of pure silver in nitric acid, and then adding to the solution some soluble chloride, such as ammonium chloride; silver chloride is then precipitated thus:—

$$Ag \mid -NO_3.\ Aq. + NH_4 \mid -Cl.\ Aq. =$$
$$Ag - Cl + NH_4 \mid -NO_3.\ Aq.$$

The silver chloride is collected on a filter, thoroughly washed, and after being dried, weighed. The Belgian chemist, **Stas**, working in this way, obtained from 108.579 grams of silver 144.207 grams of silver chloride. The relation between the atomic weight of oxygen, taken as the standard and placed equal to 16, and the formula-weight of silver chloride was ascertained by heating to redness 138.789 grams of silver chlorate, $2AgClO_3 = 2AgCl + 3O_2$; the weight of the residual silver chloride was 103.9795 grams, and that of the oxygen evolved taken as difference is 34.8095. The proportion—

Oxygen lost.		Silver chloride remaining.		$3 \times O.$		Formula weight of AgCl.
34.8095	:	103.9795	::	48	:	143.3817

gives the formula weight of silver chloride. The proportion of silver it contains is found by the equation—

$$144.207 : 108.579 :: 143.3817 : 107.9583$$

Subtracting from 143.3817 the weight of the silver it contains, 107.9583, the remainder is the atomic weight of chlorine, which, for reasons already given, is identical with its equivalent, namely, 35.4234; and 107.96 is the equivalent of silver.

Knowing these facts, the atomic weight of, say, barium may be determined by dissolving a known weight of its chloride in water, and adding to the solution a solution

of silver nitrate, so as to obtain a precipitate of silver chloride, which can be weighed, and from it the weight of the chlorine in the barium chloride deduced. Subtracting this from the weight of the barium chloride taken, the remainder is the equivalent of barium. To determine whether or not this number is identical with its atomic weight, a determination of its specific heat must be made, as described on p. 14.

In some instances the process is a more direct one. To determine the equivalent of nickel, a weighed quantity of the metal has been heated in oxygen, and the gain in weight noted. Then, as this weight is to the weight of nickel taken, so is the equivalent of oxygen to that of nickel.

These examples will suffice to give a general idea of the processes used in determining atomic weights, though, as before stated, each element requires special treatment, and the selection of the best method is often a very difficult task. It is usual, moreover, to make determinations by several methods, if that be possible, so as to avoid any permanent source of error. Many observers, too, have made such determinations, and it is not always easy to eliminate a personal element from the results which they give. An international committee publishes each year a table of atomic weights, reproduced below (with a few alterations and additions), in which the last digit of each number may in all probability be accepted as correct. A second column is added, containing the atomic volumes of the elements, so far as they are known. They represent the volumes in cubic centimetres occupied by the atomic weight of the element taken in grams, thus—197.2 grams of gold occupy 10.2 cubic centimetres. As the elements expand on rise of temperature, these results are not always comparative, but at present they are the best that can be obtained.

Table of Atomic Weights and Atomic Volumes.

		Atomic Weight.	Atomic Volume.
Aluminium	Al	27.1	10.1
Antimony	Sb	120.2	17.9
Argon	A	39.9	32.9
Arsenic	As	75.0	13.3
Barium	Ba	137.4	
Beryllium (Glucinum)	Be	9.1	4.3
Bismuth	Bi	208.0	21.2
Boron	B	11.0	4.1
Bromine	Br	79.96	25.1
Cadmium	Cd	112.4	13.0
Cæsium	Cs	132.9	
Calcium	Ca	40.1	25.3
Carbon	C	12.00	3.4
Cerium	Ce	140.25	20.8
Chlorine	Cl	35.45	
Chromium	Cr	52.1	7.7
Cobalt	Co	59.0	6.7
Copper	Cu	63.6	7.1
Erbium	Er	166	
Europium	Eu	152	
Fluorine	F	19.0	
Gadolinium	Gd	156	
Gallium	Ga	70	11.8
Germanium	Ge	72.5	
Gold	Au	197.2	10.2
Helium	He	4	
Hydrogen	H	1.008	
Indium	In	114	25.7
Iodine	I	126.97	25.7
Iridium	Ir	193.0	8.6
Iron	Fe	55.9	6.6

		Atomic Weight.	Atomic Volume.
Krypton	Kr	81.8	37.8
Lanthanum	La	138.9	22.9
Lead	Pb	206.9	18.2
Lithium	Li	7.03	11.9
Magnesium	Mg	24.36	13.3
Manganese	Mn	55.0	7.7
Mercury	Hg	200.0	14.8
Molybdenum	Mo	96.0	
Neodymium	Nd	143.6	
Neon	Ne	20	
Nickel	Ni	58.7	6.7
Niobium (Columbium)	Nb	94	14.5
Nitrogen	N	14.01	
Osmium	Os	191	8.9
Oxygen	O	16.000 (standard).	
Palladium	Pd	106.5	9.3
Phosphorus	P	31.0	17.0
Platinum	Pt	194.8	9.1
Potassium	K	39.15	45.5
Praseodymium	Pr	140.5	
Radium	Rd	225	
Rhodium	Rh	103.0	9.5
Rubidium	Rb	85.5	56.3
Ruthenium	Ru	101.7	9.2
Samarium	Sm	150.3	
Scandium	Sc	44.1	
Selenium	Se	79.2	18.5
Silicon	Si	28.4	11.4
Silver	Ag	107.93	10.3
Sodium	Ha	23.05	23.7
Strontium	Sr	87.6	34.5
Sulphur	S	32.06	15.7
Tantalum	Ta	181	17.0
Tellurium	Te	127.6	20.3
Thallium	Tl	204.1	17.2

		Atomic Weight.	Atomic Volume.
Thorium . . .	Th	232.5	29.8
Thulium . . .	Tu	171	
Tin	Sn	119.0	16.2
Titanium . . .	Ti	48.1	
Tungsten . . .	W	184	9.6
Uranium . . .	U	238.5	13.0
Vanadium . . .	V	51.2	9.3
Xenon . . .	Xe	128	35.9
Ytterbium . . .	Yb	173.0	
Yttrium . . .	Y	89.0	
Zinc . . .	Zn	65.4	9.5
Zirconium . .	Zr	90.6	21.9

Molecular Weights of the Elements.—The molecular weights of some of the elements have been successfully determined; in certain cases by their density in the gaseous state, in others by the lowering of the vapour-pressure of mercury, caused by the presence of a known weight of a dissolved metal, and again in others by the depression of the freezing-point of certain metals, caused by the presence of others in known amount. These will be considered in their order.

(*a*) **Vapour-densities.**—For reasons already explained on page 13, a molecule of oxygen is believed to contain two atoms, and inasmuch as the equivalents of most elements have been determined with reference to oxygen, by analysis or by synthesis of their oxides or of their chlorides, and as the ratio of the equivalent of chlorine to that of oxygen has been very accurately determined, it has been agreed to refer the atomic weights of the elements to the standard of oxygen instead of to that of hydrogen. But the atomic weight of oxygen is assumed as 16, and the same standard is applied to the densities of gases; instead of referring them *to the standard of* H = 1, they are referred to O = 16. To

find the molecular weights, the number expressing the density must be doubled in order to compare with the molecular weight of oxygen, which is 32.

Hydrogen.—The density referred to this standard is 1.0078. There is not yet an absolute certainty, but it is clear that the molecular weight of hydrogen must be approximately 2, *i.e.* the molecule is di-atomic.

Nitrogen.—Lord Rayleigh found the density of nitrogen to be 14.001; its molecular weight is therefore 28, and its formula N_2.

Oxygen.—Taken as 16; formula O_2. As these gases keep their relative densities up to a temperature of 1700°, it is to be presumed that they all remain diatomic, for it is much more likely that no one of them dissociates than that all dissociate to an equal extent on rise of temperature. The density of **fluorine** at atmospheric temperature is 19; the theoretical density for F_2 is 19. It follows, therefore, that fluorine, like oxygen, must consist of diatomic molecules. The case is different with **chlorine, bromine,** and **iodine.**

Chlorine at 200° was found to have the density 35.45, the same as its atomic weight, but at 1000° the density was 27.06, and at 1560° 23.3. At low temperatures, therefore, the formula of chlorine is Cl_2, but at 1560° the gas consists of 61 per cent. of molecules of Cl_1. Similar results have been found for bromine, and for iodine, which also has the formula I_2 at low temperatures, the density was found to be 63.7, corresponding to the molecular weight 127.4 at 1500° under low pressure; for reducing the pressure also increases dissociation. As the atomic weight of iodine is 126.85, the gas at 1500° consists almost entirely of molecules of I_1.

Thallium has been weighed as gas at 1730°; the density was 206.2, a sufficient approximation to 204.1 to warrant the conclusion that its molecule is diatomic.

Bismuth at 1640° gave the density 146.5, showing, as its atomic weight is 208.5, a partial dissociation from Bi_2 to Bi_1.

Phosphorus and **arsenic** give densities which indicate the presence in their gases of more complicated molecules. At 313° the density of phosphorus gas is 64, and there is a gradual decrease with rise of temperature, until at 1708° the density is 45.6. As the atomic weight of phosphorus is 31.0, the density 62 would correspond to the existence of molecules of P_4, while at 1708° there must be a considerable admixture of molecules of a smaller complexity, probably P_2. Arsenic gas had the density 154.2 at 644°, and 79.5 at 1700°; the atomic weight of arsenic being 75, the density 150 would correspond to the formula As_4, and at 1700° the molecules are almost all As_2, only a small admixture of molecules of As_4 remaining undecomposed. The density of **antimony** gas, 141.5 at 1640°, implies the presence of some molecules of Sb_4 among many molecules of Sb_2, for the atomic weight is 120.

The elements **sulphur**, **selenium**, and **tellurium** show signs of even greater molecular complexity. Dumas found the density of sulphur gas at 500° to be 94.8; now, the atomic weight of sulphur is 32.08, and 96 is 32×3; hence, it was for long supposed that a molecule of gaseous sulphur consisted of 6 atoms; but it has been recently found that at 193°, of course under a very small pressure, 2.1 mms. (for the boiling-point of sulphur at normal pressure is 446°), the density reached the high number 125.5; now, 32×4 is 128, and it must be concluded that the molecular weight of sulphur in the gaseous state is 256, and its formula at low temperatures S_8. At 800° its formula is S_2, and at 1719° the density 31.8 was found, showing no sign of further molecular simplification. Selenium, of which the atomic weight is 79.1, has the density 111 at 860°, implying some molecular complexity, and at 1420° the density is reduced to 82.2, corresponding to the formula Se_2; *and tellurium, at about* 1400°, has the gaseous density 130;

it appears, therefore, to consist of molecules of Te_2, since its atomic weight is 127.6.

These examples show that the molecules of many elements in the gaseous state are more or less complex. It is probable that sulphur, selenium, and tellurium would exist as octo-atomic molecules could the temperature be sufficiently reduced; even with sulphur at its boiling-point under normal pressure, the temperature is so high that many of these complex molecules are already decomposed. Probability is also in favour of the supposition that elements of the phosphorus group, phosphorus, arsenic, antimony, and possibly bismuth, have molecules consisting of 4 atoms; these too dissociating with rise of temperature into di-atomic molecules. Oxygen, nitrogen, and hydrogen consist of di-atomic molecules, no sign of dissociation having been remarked even at the highest attainable temperatures; but fluorine, though consisting mostly of di-atomic molecules, contains some mono-atomic ones; and chlorine, bromine, and iodine, though probably Cl_2, Br_2, and I_2 at low temperatures, dissociate into molecules identical with their atoms if the temperature is sufficiently raised. The fact of reduction in the molecular complexity of the molecules of elements prepares us for the existence of elements which in the gaseous state are already mono-atomic; and many such are known.

Mono-atomic elements.	Sodium.	Potassium.	Zinc.	Cadmium.	Mercury.
Gas-density	12.7	18.8	34.15	57.01	100.94
Temperature	Red heat	Red heat	1400°	1040°	446° and 1730°
Atomic weights	23.05	39.14	65.4	112.0	200.3
Density × 2	25.4	37.6	68.3	114.02	201.88

The presumption from these numbers is that the elements are all mono-atomic. It must be remembered that their specific heats all point to the atomic weights given.

There is, however, another argument for the *mono-atomicity of* gaseous mercury. On the assumption of the

"kinetic theory of gases," that the pressure of a gas on the walls of the vessel containing it is due to the bombardment of the sides by repeated and enormously numerous impacts of the molecules, it can be calculated that the amount of heat necessary to raise the temperature of the molecular weight expressed in grams of an ideal gas the molecules of which are supposed to be hard smooth elastic spheres, must be 3 calories, provided the gas be not allowed to expand. If, however, it be allowed to expand, it will cool itself, and more heat must be added to restore the temperature; this extra amount of heat is two additional calories. To heat the molecular weight of the gas in grams through 1°, allowing it to expand at constant pressure, requires therefore 5 calories. The "molecular heat at constant volume" is thus 3 calories; the "molecular heat at constant pressure" is 5 calories. The ratio between the two is 3 : 5, or 1 : 1.66. This has been found to be the case for mercury gas, the mono-atomicity of whose molecule is proved on other grounds; and the inactive gases of the atmosphere, helium, neon, argon, krypton, and xenon, exhibit the same ratio between their atomic heats. It therefore follows that the atoms of these gases are also identical with their molecules; and that their atomic weights are to be deduced from their densities by doubling the numbers representing the latter. Confirmatory of this view, the ratio between the molecular heats of oxygen, hydrogen, nitrogen, and gases which are known to be di-atomic, like NO, CO, &c., is as 5 : 7 or 1 : 1.4. Such gases require more heat to raise their temperature than an equal number of molecules of the mono-atomic gases do; the reason is, that the heat applied to di- or poly-atomic gases is used, not merely in transporting the atoms from place to place and raising pressure by causing them to bombard the walls of the containing vessel, but some heat is required to cause the atoms to move within the molecule, in some rotatory or vibratory manner; and consistently with this it has been found that gases consisting *of a greater number* of atoms in the molecule require still

more heat to raise the temperature of weights proportional to their molecular weights; in other words, their molecular heats at constant volume are higher the greater the number of atoms in the molecule.

For these reasons the densities of the inactive gases must be multiplied by 2 to obtain their atomic weights. The data are:—

	Helium.	Neon.	Argon.	Krypton.	Xenon.
Densities* . .	2	10	20	41	64
Atomic and molecular weights	4	20	40	82	128

(*b*) **Lowering of Freezing-Point, or Lowering of Vapour-Pressure of Solvent.**—The molecular weights of some of the elements have been determined by Raoult's method, either by the lowering of the vapour-pressure of mercury, or by the depression in the freezing-point of some other metal or solvent in which the element has been dissolved. Lithium, sodium, potassium, calcium, barium, magnesium, cadmium, gallium, thallium, manganese, silver, and gold appear to be mono-atomic, while tin, lead, aluminium, antimony, and bismuth show tendency in concentrated solution to associate to di-atomic molecules. These results were obtained by measuring the lowering of vapour-pressure of mercury produced by known weight of the metals named. By measurement of the depression in the freezing-point of tin, in which metals were dissolved, zinc, copper, silver, cadmium, lead, and mercury appeared to be mono-atomic, while aluminium was found to be di-atomic. These results, however, are not to be regarded with the same confidence as those obtained by means of measurements of the vapour-density, for it is not certain whether the molecular weight of the solvent should be taken as identical with its atomic weight. All that can be certainly affirmed is, that the molecular weights of the elements which have been placed in the same class above correspond to formulæ with the same number of atoms in the molecule. *Thus, if zinc* is mono-atomic, so is cadmium; if di-atomic,

other form. Silicon melts at a bright red heat, and can be cast into rods; they have the graphite-like crystalline form.

Tin.—This metal, when kept at a low temperature—about −30°—changes to a grey powder. On heating the powdery modification to above 20°, it is converted back into ordinary metallic tin, the more quickly the higher the temperature. If the powder be left in contact with ordinary tin at atmospheric temperature, the metal is slowly changed into its allotropic modification, and articles of tin fall to pieces.

Phosphorus.—Three forms are known for phosphorus. The first, or ordinary form, is a waxy solid, melting at 44.4°. It is soluble in carbon disulphide, and crystallises from it in rhombic prisms. It is luminous in the dark in presence of air, but if the pressure of the air be raised it ceases to shine; it is also non-luminous in oxygen. It is very easily inflamed, and burns to its oxide, P_2O_5. Phosphorus is poisonous when swallowed. The liquid obtained by melting it is nearly colourless. When this variety is heated to 240° in a vessel from which oxygen is excluded, it changes to a red substance, generally termed amorphous phosphorus. This body is insoluble in carbon disulphide and the other solvents which dissolve ordinary phosphorus. It is not luminous in the dark, and is not easily oxidisable. When heated to a temperature higher than 240°, it volatilises and condenses to ordinary phosphorus, and if air be present it takes fire. It is soluble in lead, and when the molten lead cools it crystallises out in nearly black crystals. Indeed, its colour depends on the temperature at which it is formed. If produced at 260°, it is deep red, and has a glassy fracture; at 440° it has a granular fracture and is orange; at 550° it is grey, and it fuses at 580°, and on solidifying it forms red crystals. It is possible, though not probable, that a mixture of several allotropic forms is the cause of all *these changes.*

Arsenic.—When arsenic is distilled, it passes directly

from the gaseous to the solid state on condensing. The portion which cools most quickly is a black powder; that which condenses in the warm part of the tube has a grey metallic lustre. The black variety can be converted into the crystalline metallic variety on heating to 360°. When arsenic is heated in an indifferent atmosphere under great pressure, its boiling-point is raised above its melting-point, and it melts; on solidification, it forms the metallic variety. It is also possible to obtain a yellow variety of arsenic.

Antimony.—The usual form of antimony is a white brittle metal with a faint bluish tinge. If deposited from a strong solution of its chloride by electrolysis, a grey powdery deposit is formed, which has the curious property of exploding when heated or struck; it then changes into the metallic variety. It has a lower density than the ordinary antimony.

Oxygen.—The allotropic variety of oxygen is named *ozone*; it was discovered by **Schoenbein**, and is obtained by causing a shower of minute electric sparks (the "silent electric discharge") to pass through oxygen, preferably cooled to a low temperature. One of the best forms of "ozoniser" is a tube about 1 cm. in diameter, partially evacuated, and traversed by a wire from end to end; this tube is contained in a wider one, and the space between the two tubes contains a set of metallic annuli, connected together by a wire. Oxygen is passed slowly through the space between the two tubes, while the two wires are connected with the secondary terminals of a coil; sparks pass through the inner glass and the space between the two tubes. On first passing the current the oxygen expands, but almost at once contraction ensues, and ozone issues at the further end of the tube. It is not possible, in dealing with ozone, to use indiarubber connections of any sort, for the rubber is at once attacked. Ozone is also formed when phosphorus slowly oxidises in moist air; when the vapour of ether or benzene is stirred with a hot glass rod in presence of air; when sulphuric acid acts on barium dioxide or potassium permanganate, or when sulphuric acid is electrolysed.

It is also produced in large amount when fluorine comes into contact with water.

Its name refers to its most striking property—its strong disagreeable smell. It condenses when cooled by liquid air to a dark blue liquid, which is very explosive; and its gas, when seen in a long tube, has also a blue colour; it shows characteristic spectral bands. The blue liquid boils at −106°, whereas the boiling-point of oxygen is −182°. Liquid oxygen is also blue, but has quite a pale tint. When heated to 250°, ozone is re-converted into ordinary oxygen; but oxygen cannot be transformed into ozone by heat alone. Ozone is a much more active body than oxygen; it liberates iodine from potassium iodide ($2KI.Aq + O_3 + H_2O = 2KOH\,.\,Aq + I_2 + O_2$); it oxidises metallic silver ($2Ag + O_3 = 2AgO + O_2$); it combines with metallic mercury; and it changes lead sulphide into sulphate ($PbS + 4O_3 = PbSO_4 + 4O_2$). When passed through a solution of hydrogen dioxide, oxygen is evolved ($H_2O_2\,.\,Aq + O_3 = H_2O\,.\,Aq + 2O_2$); and it bleaches indigo and other colouring matters.

Its density is 24, that of oxygen being 16; whence its formula is O_3. Its rate of diffusion into air bears to that of chlorine, of which the density is 35.47, the ratio of $\sqrt{24} : \sqrt{35.5}$—another proof of its density. When oxygen is converted into ozone, the portion which is changed contracts in the proportion 3 : 2; and conversely, when ozone is heated and converted into oxygen, that portion of the gas which consists of ozone increases in volume from 2 : 3. All these proofs demonstrate that the formula of ozone is O_3.

Ozone is a poison; it excites coughing, and in large quantity asphyxiates, the blood becoming venous. It is very doubtful whether ozone has been found in the atmosphere, except, perhaps, after a thunderstorm.

Sulphur.—The allotropy of gaseous sulphur has already been alluded to; that of liquid and of solid sulphur is no less striking. When sulphur is melted, it forms a mobile, light brown liquid. On raising the temperature, the liquid be-

comes viscous, so much so, indeed, that the vessel containing it can be inverted without spilling the liquid; and at a still higher temperature it again becomes mobile, but has a deep brown colour. On cooling, these changes are reversed. If viscous sulphur be poured into water, it hardens to a substance resembling indiarubber; this form, if kept for some hours, falls into minute octahedral crystals. When molten sulphur is allowed to cool slowly, it solidifies at 120°, forming long monoclinic needles of a pale brown colour. This variety is also deposited on evaporating a solution of sulphur in ether or in benzene. These needles, on standing for a few hours, become opaque and spontaneously fall into minute rhombic octahedra. Octahedral crystals of a large size may be produced by allowing a solution of sulphur in carbon disulphide to evaporate spontaneously; this variety melts at 115°; its colour is bright yellow; it is in this form that sulphur occurs native. Its density is 2.07, whereas that of monoclinic sulphur is 1.97 at 0°. Two other varieties of sulphur are known. If sulphur vapour be quickly cooled, it condenses in a dusty form, termed "flowers of sulphur;" this powder, if treated with carbon disulphide, leaves an insoluble residue, distinct from all other forms, which are all soluble in disulphide. And lastly, if sulphur be produced in presence of water by the decomposing action of water on sulphur chloride, or by the action of hydrogen dioxide on hydrogen sulphide, the sulphur does not separate, but remains in a state of "pseudo-solution" in the water; it can be precipitated on addition of salts such as calcium chloride. It is thus evident that the chemistry of the element sulphur is very complicated.

Selenium.—This element has three allotropic forms; when precipitated from selenious acid by sulphurous acid—$H_2SeO_3.Aq + 2H_2SO_3.Aq = Se + 2H_2SO_4.Aq + H_2O$—it forms a red powder, soluble in carbon disulphide, and crystallising therefrom in dark red crystals, a non-conductor of electricity. Either the amorphous red variety or these crystals, if kept at 210° for some time, change into a black

crystalline variety, insoluble in carbon disulphide, and conducting electricity on exposure to light. These varieties also differ in density and melting-point.

Ruthenium, Rhodium, and **Iridium** are grey-white metals, hard and fusible only at a very high temperature. They are insoluble in hydrochloric, nitric, or sulphuric acid. On alloying them with zinc or lead, and then dissolving out the alloyed metal with acid, the ruthenium, rhodium, or iridium is left as a black powder, exploding when gently warmed, and going back into the ordinary form of the metal.

Iron.—It has been known for many centuries that the properties of iron are profoundly modified when it contains a small percentage of carbon; it is then termed **steel.** Steel has a fine granular fracture, and is not fibrous like pure wrought iron, or coarsely crystalline like cast-iron, which contains a greater proportion of carbon than steel, the latter containing from 0.8 to 1.9 per cent. When steel is heated and then suddenly cooled,—an operation termed "tempering,"—it becomes very hard; this is due to a change which takes place in the molecular structure of iron at 850°. At that temperature its specific heat suffers a considerable change; and if the iron contains a small percentage of carbon, the allotropic state persists after the cooling has taken place, if produced sufficiently rapidly. The various qualities of steel, elastic as in springs, hard as in razors, brittle and extremely hard as in files, are due to admixture of more or less of the allotropic modification with ordinary iron, which is a comparatively soft metal.

Silver and **Gold.**—Several metals, among them silver, gold, and platinum, when precipitated from aqueous solutions of their salts by some reducing agent, such as sodium formate, form apparent solutions of the metal in water. That of platinum is grey, of silver blue or red, and of gold purple. The colour, however, depends on the state of division of the metal, and it may vary greatly with the *same metal. If the* "pseudo-solution" of platinum is

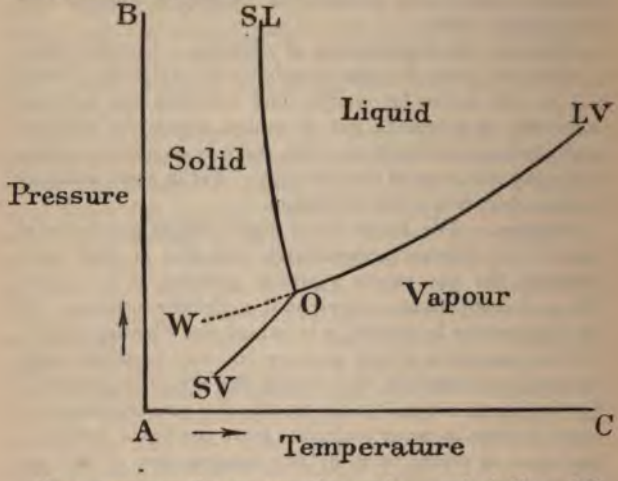
warmed, the metal is precipitated as a black powder, known as "platinum-black." This substance readily absorbs gaseous oxygen or hydrogen; when heated, it is converted into a grey powder, obviously finely divided ordinary platinum, termed "platinum sponge." On evaporating the pseudo-solutions of silver or gold, the metal remains as a coloured residue; on warming or rubbing, it changes into the ordinary metal.

These are the known cases of allotropy. In some cases, as when the gases of ozone or sulphur are weighed, a direct clue to the molecular weight, and therefore the cause of isomerism, is revealed; but in others, where the different modifications are liquid or solid, there is no obvious means of tracing the cause of the allotropy. Yet in some instances a reasonable theory can be formed.

Phases.—We know that a liquid and its gas can exist together at different temperatures, and that at high temperatures the gas exerts a greater pressure than at low. To each temperature corresponds a definite pressure. If the temperature be named, it is termed the "boiling-point" at that pressure; if the pressure for any particular temperature be alluded to, it is called the "vapour-pressure." According to the molecular theory, the vapour-pressure is reached when as many molecules leave the liquid surface in unit time as return to it by the condensation of the gas. There is a state of equilibrium; but on raising the temperature the equilibrium is disturbed, and more vapour is given off to restore it. The gaseous state and the liquid state are termed two **phases** of the same kind of matter, and they can coexist at various temperatures.

When the pressure is reduced below a certain amount —for water to 4.6 mms.—the boiling-point is lowered to 0°. At this temperature water usually freezes under a pressure of one atmosphere. As the pressure is 4.6 mms., the freezing-point of the water will be at 0.007° above zero; for it is found that the freezing-point of water is *lowered by* that amount for each rise of one atmosphere

pressure; and if the atmosphere pressure be removed, the freezing-point will be raised. At this temperature, therefore, ice, water, and water-vapour are all in equilibrium with each other and can coexist. The point is called the "triple point." The states of water, ice, and steam can be represented by a diagram.



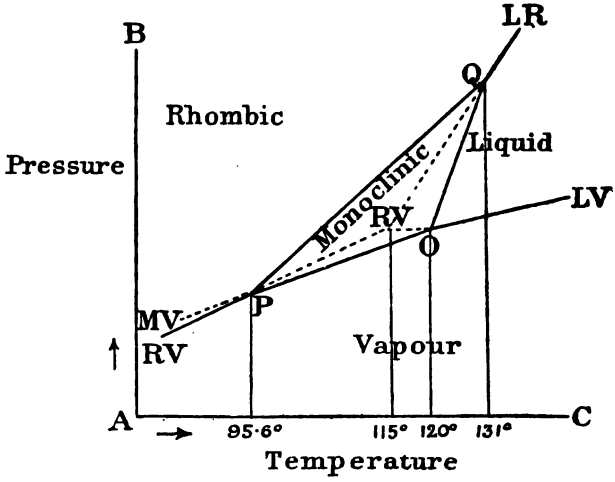
Let pressures be measured up the vertical line AB, and temperatures along the horizontal line AC. The point O corresponds to the temperature 0.007° and to the pressure 4.6 mms. Along the line OLV (LV standing for liquid-vapour) the liquid and the vapour can coexist; it is usually termed the "vapour-pressure curve." The line O SL (solid-liquid) shows the alteration in the melting-point of ice as the pressure rises; its slope is greatly exaggerated in order to make it visible. It shows that as the pressure is raised the melting-point of ice becomes lower and lower. *Lastly, the line OSV* (solid-vapour) indicates the coexist*ence of the solid* and the vapour phases; the pressure is

below 4.6 mms., and the temperature below 0°. The regions shown correspond to those conditions of temperature and pressure where the substance can exist as solid, as liquid, or as gas. The dotted line WO represents the condition of a super-cooled liquid. It is possible to cool water below 0°; for example, if it be pure and kept at rest, its vapour-pressure is then greater than that of ice at the same temperature. It has not been found possible to heat ice above its melting-point without its melting, but it is possible to cool steam somewhat below its condensing temperature without condensation occurring. These states of relative instability have been called "metastable." Shaking the water or introducing particles of dust into the steam at once induce freezing or condensation; the water changes to ice or the steam condenses.

The condition of allotropy can be similarly represented. But the problem is more complicated; in the case of sulphur, for example, there are two solid phases, the rhombic and the monoclinic, besides more than one liquid phase. As the two solid phases, the rhombic melting at 115°, and the monoclinic melting at 120°, are well known, attention will be confined to them.

If sulphur be allowed to crystallise from fusion, it assumes the monoclinic form of long prisms. These crystals, however, change spontaneously at the ordinary temperature, and in a few hours fall into minute rhombic octahedra. At the temperature 95.6°, however, this change no longer takes place; the two crystalline forms can coexist in presence of each other without one form turning into the other. The rhombic variety gives off vapour which of course exerts pressure at that temperature and at lower temperatures at which the rhombic variety is stable; and the vapour-pressure curve is indicated by the line PRV (rhombic-vapour). This temperature is termed the "transition temperature" for rhombic and monoclinic sulphur and sulphur-vapour. It may be compared with the melting-*point of ice* under 4.6 mms. pressure, which, it will be

remembered, is 0.007°, where water, ice, and steam are in equilibrium. But it differs inasmuch as it is possible to heat rhombic sulphur above the transition-point P without immediate change. PO is the vapour-pressure curve for monoclinic sulphur, which melts at 120°; and each of these curves must meet in the transition-point P, for at that temperature both modifications can coexist. Below 95.6 the monoclinic form is in the metastable condition, and the line



PMV, which is a continuation of the line OP, expresses the vapour-pressure of the monoclinic variety below the transition temperature. The rhombic variety above 95.6° is in the metastable condition, and its vapour-pressure is shown by the line PRV, the upper portion of which is dotted. If the sulphur be compressed, the transition-point rises, and the line PQ typefies this. At 120° there must be *another transition*-point, for here rhombic sulphur, liquid *sulphur, and sulphur*-vapour may exist in presence of each

other. Now the melting-point of sulphur is raised by pressure instead of being lowered, as in the case of water. This is the more usual; the lowering of melting-point of the solid water depends on the fact that the density of ice is less than that of water, but that of solid sulphur is greater than that of molten sulphur. Hence the rise of the transition-point along the line PQ. At O three curves meet: OP, representing the vapour-pressure of monoclinic sulphur; O LV, the vapour-pressure of liquid sulphur; and OQ, the effect of pressure in raising the melting-point of rhombic sulphur. The lines PQ and OQ happen to meet at Q, which is also a transition-point; it lies at 131°; and here rhombic, monoclinic, and liquid sulphur can all coexist, though the pressure is too high for vapour to exist along with them. At higher temperatures and pressures monoclinic sulphur is incapable of existence. As we have seen, the metastable states of sulphur are capable of existence for some time. Rhombic sulphur can be heated to its melting-point, 115°, which lies above its transition temperature. At this temperature it and the liquid resulting from its fusion are both in a metastable condition. And the effects of pressure in raising the melting-point of rhombic sulphur is shown by the dotted line RVQ, which is continued in QLR (liquid-rhombic) at temperatures at which the monoclinic variety is no longer capable of existence.

Although the allotropy of other elements has not been so minutely studied as that of sulphur, it is certain that the various conditions can all be represented in a similar manner. For example, the transition-point of the grey and metallic modifications of tin is 20°; below that temperature metallic tin is in the metastable condition; if cooled sufficiently, it may change spontaneously into the grey powder, but the change may not take place, just as water may be kept super-cooled without freezing. But just as the addition of a crystal of ice to super-cooled water causes it to *crystallise*, so the contact of grey tin below 20° with

metallic tin induces the change; the surface of the tin becomes covered with spots like pimples, and, if time be given, all the tin falls to powder. The change is the more rapid, up to a certain point, the lower the temperature. If the grey tin be raised in temperature above 20°, it is reconverted into metallic tin, the more quickly the higher the temperature.

The yellow waxy condition of ordinary phosphorus, too, appears to be a metastable condition, for if its temperature is raised under pressure, red phosphorus is produced. On the other hand, if red phosphorus be heated under ordinary pressure, it volatilises and condenses as yellow phosphorus. Nevertheless, at the very highest temperatures, the vapour-pressure curves would indicate that yellow phosphorus is the stable form.

We are still in the dark as to the precise reason of such allotropic changes. From cases which can be investigated, owing to the liquid or gaseous states of the allotropic modifications, the cause would appear to consist in a greater or less molecular complexity, but this is not proved for solids. It is possible that the cause of allotropy is to be found, in some cases at least, in a different arrangement of the molecules in the solid, and this suggestion falls in with the fact that allotropy often consists in different crystalline forms, but it is also conceivable that a different crystalline form may correspond with difference in molecular complexity as well as with different molecular arrangement. Until some method is discovered whereby the molecular weights of solids can be determined, it is not probable that certainty will be attained.

CHAPTER VI

Isomerism—Polymerism—Optical and Crystallographic Isomerism—Stereo-Isomerism—Tautomerism.

Closely connected with allotropy is what is termed **isomerism.** Attention was first called to the existence of compounds with identical composition, so far as it could be ascertained by analysis, but possessing different physical properties, such as melting-point, boiling-point, and crystalline form, and different chemical properties, by **Wöhler** and by **Liebig.** **Faraday,** too, drew attention to a similar phenomenon which has received the name of **polymerism.**

All food contains the elements carbon, hydrogen, oxygen, and nitrogen, besides sulphur, phosphorus, and other elements. The main constituents of food are starch, which is the chief component of bread, and which is devoid of nitrogen; and albumen and allied bodies, of which flesh mainly consists, which is rich in nitrogen; dried meat, indeed, contains from 10 to 12 per cent. of that element. During the passage of food through the system, the carbon and hydrogen are mainly eliminated by the lungs as carbon dioxide, CO_2, and water, H_2O; while the largest portion of the nitrogen passes away through the kidneys, in the form of a compound named **urea,** of the formula CON_2H_4. Now Wöhler succeeded in 1827 in forming urea artificially by preparing a compound of ammonia, NH_3, with an acid termed *cyanic acid, HNCO,* itself producible from the elements which

it contains. On heating this compound, ammonium cyanate, NH_4NCO, to the temperature of boiling water, it undergoes an "isomeric change." Before such heating, if the ammonium cyanate be warmed with a solution of caustic potash, the smell of ammonia is at once apparent; this is the usual test for ammonium ions; but after the change into urea has taken place, ammonia is not revealed by this test. Moreover, the compound formed, urea, forms salts with acids; it unites with hydrogen chloride, for example, forming $CON_2H_4.HCl$. The compound from which it is derived, ammonium cyanate, on treatment with hydrochloric acid, is converted into ammonium chloride, NH_4Cl, and cyanic acid, which itself undergoes further change, unnecessary to allude to here:—

$$NH_4NCO + HCl.Aq = NH_4Cl.Aq + HNCO.$$

It is evident that here there are two compounds containing the same elements in the same proportion by weight, and yet having very different properties.

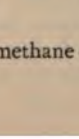
Faraday, in experimenting with oil-gas, produced by heating the vapour evolved from oil at a high temperature, attempted to condense it to a liquid by application of cold and pressure. In this he was successful, and the compound he obtained was identical in composition with the well-known olefiant gas, now termed ethylene, C_2H_4, which is the product on heating a mixture of alcohol with concentrated sulphuric acid. But Faraday's product possessed a density twice as great as that of ethylene. While ethylene has a density approximately 14 times that of hydrogen, implying the molecular weight 28 (and $C_2 = 24 + H_4 = 4$ are together equal to 28), Faraday's gas, which is now known as butylene, was found to have the density 28, implying a molecular weight of 56, and involving the formula C_4H_8. Hence it appeared that two compounds could exist, of which one might possess a molecular weight twice as great as the other, yet of the same percentage composition; and to this the name polymerism was applied; the substance

of higher molecular weight is termed the polymer of that of the simpler molecule.

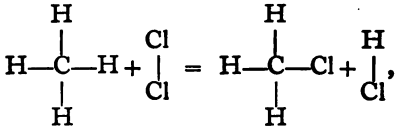
It is chiefly among compounds of carbon that the phenomena of isomerism and polymerism have been observed; although there are some well-marked cases of the latter among compounds of other elements; the best known is that of NO_2 and N_2O_4; the former, which exists only at a high temperature, is a dark red gas; the latter is almost colourless, and is produced by cooling the former. But in this case the two compounds, to both of which the name nitric peroxide is applied, are very easily transformed from one state into the other, and do not differ in their chemical reactions. Instances of isomerism among compounds of elements other than carbon are rare, but are not unknown.

The explanation of this curious phenomenon was sought for in the arrangement of the atoms in the molecule. The cases given, although they were the first noticed, are not the simplest; an instance will therefore be chosen from compounds containing only the two elements carbon and hydrogen.

One of the constituents of coal-gas is named **methane**, or **marsh-gas**; it escapes from the mud at the bottom of stagnant pools when it is stirred with a stick; its formula is CH_4. This gas, when mixed with its own volume of chlorine, and exposed to diffuse light for some hours, exchanges one of the atoms of hydrogen which it contains for an atom of chlorine; at the same time the displaced hydrogen unites with another atom of chlorine, forming hydrogen chloride, thus: $CH_4 + Cl_2 = CH_3Cl + HCl$. If it be assumed that the hydrogen in marsh-gas is in union with the carbon, and that that union can be pictured by a stroke or "bond" between the atoms (see p. 58), the formula of



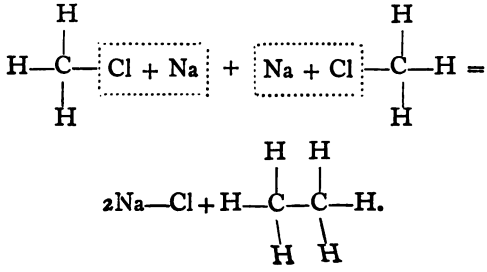
methane can be written H—C—H, and the above equation—



on the similar assumption that a molecule of chlorine consists of two atoms, of which one replaces hydrogen in methane, while the other unites with that displaced hydrogen to form H—Cl.

Now only one compound of the formula CH_3Cl is known; hence it may be argued that the hydrogen atoms and the chlorine atoms are symmetrically grouped round the carbon atom in chloromethane—for so the compound is termed.

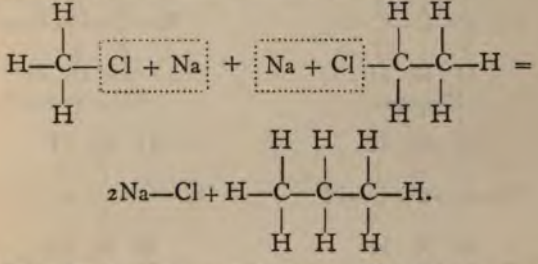
The element sodium readily reacts with chlorine; indeed, if hot sodium be plunged into a jar of chlorine gas, the metal burns brightly, and a white compound of the two is produced, which is none other than common salt, or sodium chloride, NaCl. It is possible to withdraw the chlorine from chloromethane by bringing the gas, dissolved in ether (on which neither it nor sodium have any action) in contact with chips of sodium. Another gas is produced, of which the analysis and vapour-density show it to possess the formula C_2H_6; and it is reasonable to suppose that it has been produced by the union of the two groups, CH_3, left after the removal of the atom of chlorine from CH_3Cl; this change can be thus expressed:



The new gas is called **ethane.** It, too, exists in only one modification, and it is legitimate to suppose that the atoms of hydrogen are symmetrically arranged with reference to the two atoms of carbon.

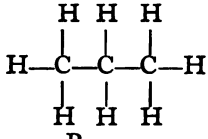
Like methane, it can be attacked by chlorine with similar results; the equation is: $C_2H_6 + Cl_2 = C_2H_5Cl + HCl$. And here again only one chlorethane, C_2H_5Cl, is known; another argument in favour of symmetry.

If a mixture of chloromethane and chlorethane, dissolved in ether, be treated with sodium, a third "hydrocarbon" is formed, possessing the formula C_3H_8; it is named **propane.** Its formation may be expressed thus:

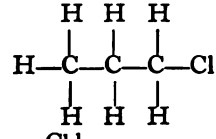


Again, only one propane is known. But if it is exposed to the action of chlorine, two monochloropropanes are formed, each of which has the empirical formula C_3H_7Cl. The chlorine atom in each isomer may be replaced by the hydroxyl group, $-OH$; the resulting products, C_3H_7OH, are termed **propyl** and **isopropyl alcohols.** It is possible to reconvert each of these compounds into its respective chloropropane; and it is also possible to obtain from them, by oxidation, very different products. Propyl alcohol, when oxidised by boiling with a solution of chromic acid, a compound which easily loses oxygen, is converted first into propionic aldehyde, C_3H_6O; but on continued oxidation the aldehyde is changed to propionic acid, $C_3H_6O_2$. *On the other hand,* isopropyl alcohol is oxidised by similar

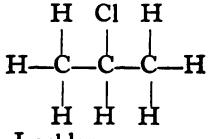
treatment to a compound called acetone, possessing the same empirical formula as propionic aldehyde, viz., C_3H_6O, but differing entirely from the latter in properties; and if the process of oxidation be continued, the acetone is broken up into acetic acid and carbon dioxide, both simpler compounds, containing fewer atoms of carbon than acetone. These changes are easily represented by the following formulæ, which are termed *graphic*, or *structural*, or *constitutional*, inasmuch as they represent to some extent the structure of each molecule.



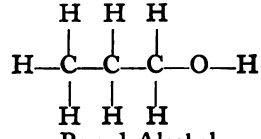
Propane.



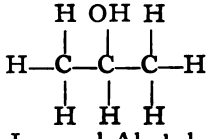
Chloropropane.



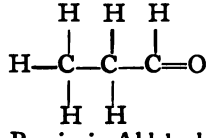
Isochloropropane.



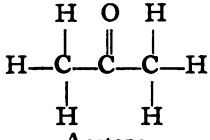
Propyl Alcohol.



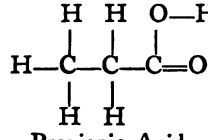
Isopropyl Alcohol.



Propionic Aldehyde.



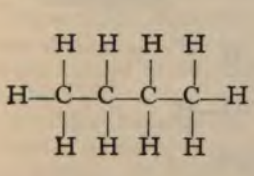
Acetone.



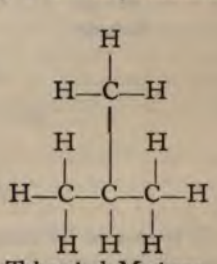
Propionic Acid.

It is evident that while propane itself is a symmetrical substance, inasmuch as all the atoms of hydrogen are symmetrically arranged as regards the three atoms of carbon, as soon as an atom of hydrogen is replaced by an atom of chlorine, two possibilities are open; the atom of chlorine may attach itself either to one of the end atoms of carbon, or to the middle one. In each case a different compound is produced; and this is shown not only by the different boiling-points of the two chloro-compounds, but also by their behaviour with reagents.

The relation of propane to ethane may be conceived to be due to the replacement of an atom of hydrogen in the latter by the group $-CH_3$, which is termed the *methyl group*. Ethane may be viewed as methyl-methane, $H_3C—CH_3$, and propane may also be regarded as di-methyl-methane, $H_3C—CH_2—CH_3$, the central group $—CH_2—$being taken as the methane molecule, of which two atoms of hydrogen have been replaced by two methyl groups. If the structural formula of propane be again inspected, it is evident that two butanes must be possible—one, a methyl-propane; the other, a trimethyl-methane, thus:—



Methyl-Propane.



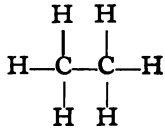
Trimethyl-Methane.

These two butanes may yield similar derivatives. It is evident on inspection that the first will furnish two monochlorobutanes; one, if an atom of chlorine replaces *one of hydrogen* of either of the two end atoms of carbon;

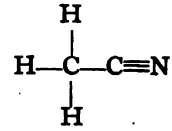
the other, if the chlorine atom is attached to either of the middle atoms of carbon. And the second butane can also yield two chlorobutanes, according as a chlorine atom replaces hydrogen of one of the three $-CH_3$ groups, or hydrogen of the $\equiv CH$ group.

Such forms of isomerism are very common, and instances might be multiplied indefinitely.

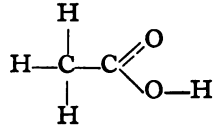
Another form of isomerism arises when an element such as nitrogen, which has more than one valency, is contained in the molecule. The atom of nitrogen can be made to occupy one of two positions as regards an atom of carbon. A common instance of this is the isomerism of the *nitriles* and the *carbamines*. A nitrile is a compound in which an atom of nitrogen replaces three atoms of hydrogen, all of which were attached to the same atom of carbon. Thus, from ethane, C_2H_6, acetonitrile is derived thus :—



Ethane.

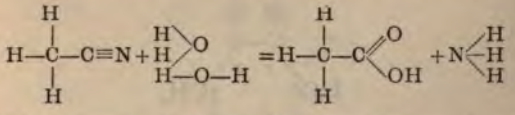


Acetonitrile.

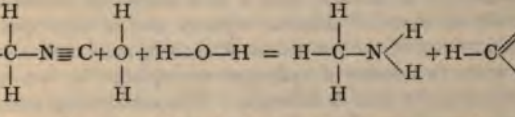


Acetic Acid.

It is seen to be closely allied to acetic acid, in which three of the atoms of hydrogen of ethane are also replaced; but this time two by an atom of oxygen, and the third by the hydroxyl-group, $-OH$. This close connection is made obvious by boiling the acetonitrile with dilute alkali; the nitrogen is evolved as ammonia, while oxygen and hydroxyl *take the place of* the atom of nitrogen :—



But an isomer of acetonitrile is also known, to which the formula $CH_3N{\equiv}C$ is ascribed; for, on causing it to react with water, the products are methylamine, $CH_3{-}NH_2$, and formic acid, $HC{\overset{O}{\diagdown}}{\diagup}{\overset{}{OH}}$, thus :—

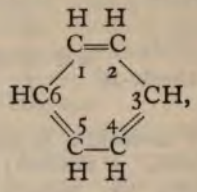


From this it is inferred that in the latter case the atom of nitrogen is in direct union with the atom of carbon of the CH_3 group; it remains united even after attack by water in presence of acid, the latter accelerating the action.

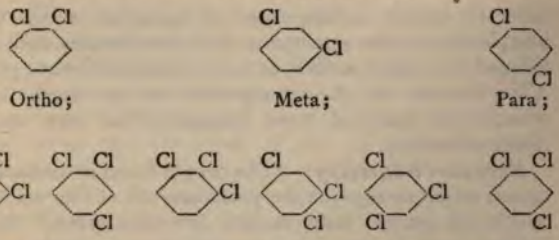
From these instances it is evident that the *position* of the elements or groups in a molecule, as well as the composition of the molecule, determine its nature; and this fact is even more strikingly shown by isomerism in the group of compounds related to benzene, a liquid hydrocarbon of the formula C_6H_6.

It is found that when this compound is attacked by chlorine, so that an atom of hydrogen is replaced by an atom of chlorine, the resulting oily liquid, named chlorobenzene, having the formula C_6H_5Cl, exists in only one modification. But if two atoms of hydrogen are replaced by two atoms of chlorine, there are three compounds produced, to each of which the empirical formula $C_6H_4Cl_2$ may be ascribed. To what is this isomerism due?

The generally accepted graphic or structural formula for benzene, *first* suggested by **Kekulé**, formerly professor of *chemistry at Bonn*, is—



in which the six atoms of carbon are arranged as a ring, and each in combination with one atom of hydrogen. Bearing in mind that a symmetrical replacement cannot produce isomerism, it is obvious that it is a matter of indifference whether an atom of chlorine replaces one of hydrogen attached to any of the six atoms of carbon, numbered 1 to 6. But when two atoms of hydrogen are replaced by two atoms of chlorine, the case is different. The substituting atoms of chlorine may have three distinct positions relatively to each other; they may replace hydrogen atoms combined with the carbon atoms 1 and 2, or with 1 and 3, or, lastly, with 1 and 4. Obviously the numbering 1 and 2 expresses only any two contiguous atoms; it is identical with 2 and 3, 3 and 4, &c. So, too, 1 and 3 is identical with 2 and 4, 3 and 5, &c.; and 1 and 4 is the same as 2 and 5 or 3 and 6. These chlorine derivatives may be converted into numerous others by replacing the atoms of chlorine by other atoms or groups of atoms; and so three series of compounds are obtainable, all of which belong to three separate groups. It has been found possible to determine the positions relative to each other of the entering atoms by the following ingenious device. Expressing, for shortness' sake, the structural formula above given by a simple hexagon, and assuming that carbon atoms are situated at the angles of the hexagon, and, where not otherwise indicated, in combination with hydrogen; but indicating by the symbol Cl that an atom of hydrogen has been replaced by one of chlorine, we have the *following three formulæ* for the three dichlorobenzenes:



Now, if each of these compounds be separately treated with chlorine, trichlorobenzenes are formed; these are shown in the lower line; and it will be noticed that while the first dichlorobenzene (that designated by the prefix "ortho-") can yield two, and only two, trichlorobenzenes, the "meta-" dichlorobenzene may yield three trichlorobenzenes, but the "para-" dichlorobenzene only one; or in numbers, 1 2 may yield 1 2 3 and 1 2 4 trichlorobenzenes; 1 3 may yield 1 2 3, 1 3 4, and 1 3 5 trichlorobenzenes; while 1 4 dichlorobenzenes can yield only 1 2 4 trichlorobenzenes; the last is obviously identical with 1 3 4, or with 1 4 5, or with 1 4 6 trichlorobenzene. In this way the actual position of the chlorine atoms, relatively to each other, in the three dichlorobenzenes, was established.

All these formulæ, it will be noticed, are written on the assumption that the atoms of the elements lie in a plane. Now this assumption is exceedingly improbable. It is true that a map represents only the length and breadth of a country; not the height of the mountains, unless contour lines be made use of. And yet a map renders great service, for we use it, allowing for this important omission. So these structural formulæ may be advantageously employed, so long as we remember that they do not represent *all* the structure. This fact must have been in the minds of many chemists for more than ten years before **J. A. LeBel** and **J. H. van't Hoff** pointed out independently, in 1874, *the necessity* of employing formulæ of three dimensions in

order to explain certain cases of isomerism which were inexplicable on the assumption that the elements were distributed on a plane surface, as in the instances already given. This doctrine of the arrangement of the atoms of a molecule in space of three dimensions has been termed Stereo-chemistry.

Stereo-chemistry.—The deposit found in wine-casks, named *tartar* or *argol*, is the potassium salt of four acids, to which the generic name *tartaric* has been given. But it has long been known that although all these acids are represented by the formula $C_4H_6O_6$, they differ in physical properties. In order to understand the nature of this difference, a short explanation must be given of the nature of *polarised light.*

A mineral named tourmaline is known, which is sometimes used as a gem. Its colour is usually green, and it occurs in fairly large transparent crystals. If a slice of this mineral be cut, it is to all appearance quite transparent, allowing light to pass with only a slight diminution in its intensity, as would be the case if the light were to pass through a plate of somewhat dull greenish glass. Through two parallel plates of tourmaline, if held in a certain position, light still passes with scarcely diminished intensity; but if the one plate be slid round on its neighbour, so that it has performed a partial revolution of 90°, the two plates in this position are no longer transparent, but cut off light and become practically opaque. The light, after passing through the first plate, is said to be polarised; and it is possible to extinguish this polarised light by interposing a second plate placed in a certain position.

It is now certain that the phenomena of light are to be attributed to the propagation of waves in a fluid which penetrates all space, even the interior of solids; a fluid without weight, possibly composed of particles, which, however, must not be confused with the atoms or molecules of ponderable bodies. This fluid is termed *ether*. Now waves may be caused in ether by other agencies than

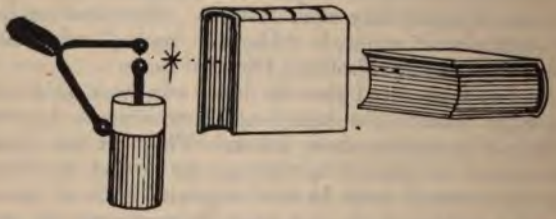
light. When an ordinary Leyden jar is discharged, the process of discharging it is not instantaneous; the spark which passes between the knob of the electrical "tongs" used to discharge it and the knob of the jar is merely one of a number which pass to and fro between the knob of the tongs and the knob of the jar until electrical equilibrium is established. The passage of such sparks causes waves to be propagated through the ether, waves which differ from those of light only in their much greater length. Such waves, whether of light or of electric disturbance, are propagated at right angles to the direction of their oscillation; they resemble waves on the sea in this respect, but differ inasmuch as sea-waves oscillate merely up and down, whereas these waves of light or electric disturbance oscillate in all possible directions at right angles to that in which they move forward. The name applied to such electric waves is "Hertzian waves," after their discoverer, the late Professor Hertz of Bonn.

It has been found that the leaves of a book held with its edge towards the source of electric waves has the effect of polarising these waves. They are not much diminished in intensity by their passage through the book, and if a second book be held edgewise, with its leaves parallel to those of the first book, the waves can still pass on. But if the one book be turned round so that its leaves are at right angles to those of the other, the electric waves are blocked, and are no longer able to pass. The Hertzian waves are so long, and are made in such a manner, that it is possible to ascertain in which plane they are oscillating; indeed, the experiment with the book proves this. For it is known that if the plane of the waves coincides with that of the pages of the book, the waves are annihilated; they cause electrical currents in each leaf, and are thus absorbed. But as each leaf is separated from its neighbour by a thin layer of air, which is a practical insulator of electricity, if the leaves of the book are turned at right angles to the position in which they annihilate the electric waves, these

waves cannot excite currents in the leaves, because each leaf is insulated from its neighbour, and the currents have no scope. After passage through the book, those waves which were originally oscillating in the plane of these leaves are annihilated, and used up in inciting feeble electric currents in each leaf, while those waves originally at right angles to the plane of the book's leaves pass through. Waves oscillating in intermediate planes, *e.g.* at an angle of 45° to the plane of the leaves, are partly annihilated, and partly pass, in proportion to the angle which they make.

The coarsely foliated structure of a book, it cannot be doubted, is analogous to the structure of a plate of tourmaline. It is also almost certainly foliated, but the foliations

FIG. 4.



are extremely minute, so that the influence they have in transmitting or obscuring light waves is commensurate with the difference in the oscillation-length of light waves and Hertzian waves. The light which has passed through tourmaline, like the electric waves which pass through the leaves of a book held edgewise, has this peculiarity—*the waves oscillate in one plane*, and resemble in that respect the waves of the sea. They are said to be polarised.

Now it has been found that certain substances, such as crystals of quartz or of chlorate of potassium, have the curious property of rotating the plane of oscillation of *polarised light*; that is, light polarised by passage through *a plate of tourmaline* (or by other means, for there are

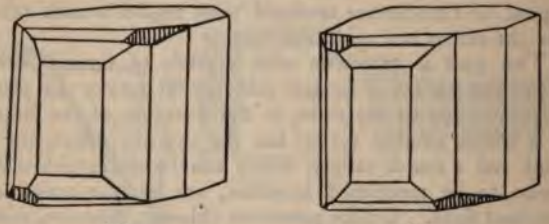
more convenient plans for polarising light), and then transmitted through a plate of crystallised potassium chlorate, is not wholly obscured when it impinges on a second plate of tourmaline held at right angles to the first; it is necessary to turn the second tourmaline through more than a right angle in order that total obscuration shall result. The plane of polarisation is *rotated* by the chlorate crystal. If, however, the crystal is dissolved in water, its solution has no such property; and it is inferred that the rotation is due, not to any arrangement of the atoms in the molecule of chlorate, but to the arrangement of the molecules in the crystal. For if the rotation were due to the former cause, it would be produced by the solution as well as by the solid. It is believed, therefore, that the molecules in a crystal of chlorate are arranged with regard to each other like the stones in a spiral staircase.

The case is otherwise with crystals of tartaric acid. While one variety of tartaric acid crystal rotates the plane of polarisation to the right, in the direction of the hands of a watch, another variety has the opposite effect, and a third and a fourth variety, which can be distinguished by means to be mentioned hereafter, are without action on polarised light. Unlike potassium chlorate, however, solutions of these crystals of tartaric acid have the same effect as the crystals themselves; those which have a right-handed rotatory power retain that power even when dissolved; the left-handed ones remain left-handed, and the neutral ones neutral.

In 1861, **Louis Pasteur**, at that time assistant to Professor Balard, of Paris, made a most important discovery. It was that crystals of dextro-rotatory or right-handed tartaric acid, which had hitherto been believed to be regular, were all characterised by small facets, developed only on one corner. The neutral tartaric acid, known as racemic acid, had no such facets; but on crystallising a certain double salt of racemic acid containing ammonium and sodium, Pasteur discovered that two kinds of crystals

were deposited; some with facets on the right upper corner (see (*a*) Fig. 5), and some with facets on the left corner. The facets in question are shaded in the figure. And most singularly, the crystals, after they had been picked out and separated from each other, when dissolved in water each rotated the plane of polarised light, the crystals with right facets to the right, those with left facets to the left. Up to that time only the dextro-rotatory tartaric acid had been known. From this Pasteur drew the inference that the difference between the two varieties must be due to the different arrangement of the atoms in the molecules of the two varieties of tartaric acid in space of three dimensions.

FIG. 5.



(*a*) (*b*)

Pasteur also devised two other methods of separating the two varieties of tartaric acid contained in racemic acid: one was by preparing a salt of racemic acid with a base such as quinine, which itself possesses optical properties. The salt of dextro-tartaric acid with this base is much more soluble than that of the left-handed or lævo-rotatory tartaric acid; so that the crystals which separate out on evaporating the solution are practically pure lævo-tartrate. His other method of effecting the separation, or, in this case, the destruction of the dextro-tartrate, was by allowing a solution of racemate of ammonium to mould. The organism consumes *the dextro-tartrate*, and the lævo-tartrate remains after the *mould has been* suffered to grow for a sufficient time. It

is only the dextro-compound, in fact, which serves as food for the mould.

In 1874, LeBel and van't Hoff independently propounded a theory to explain these and similar cases of isomerism; it is based on the conception that all molecules occupy space of three dimensions, and that the isomerism is caused by the different arrangement of the atoms in the molecule. This arrangement also gives a clue to the behaviour of such isomers in rotating the plane of polarised light to the left or to the right, and also indicates why crystals composed of such molecules should develop "hemihedral" facets, as those represented on only one side of a crystal are termed.

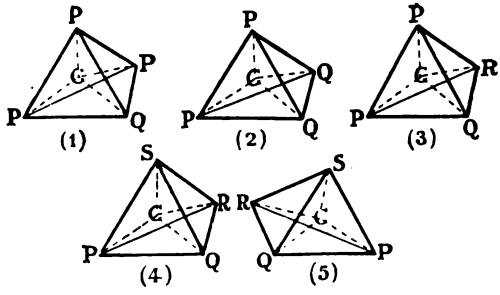
It is not necessary to consider any particular compound in giving a sketch of this theory; it may be stated in general terms.

Marsh-gas, or methane, it has already been remarked, has the formula CH_4. We have already seen that one of the four atoms of hydrogen which it contains may be replaced by an atom of chlorine, and the chlorine by the group CH_3, or methyl. It is possible to replace successively all four atoms of the hydrogen of methane by atoms or groups; these may be all different. If we indicate such atoms or groups by the letters P, Q, R, S, we may have the compounds CP_3Q, CP_2Q_2, CP_2QR, and $CPQRS$, as well as CP_4. The stereo-chemical hypothesis is based on the conception that the carbon atom is situated at the central point of a pyramid built on a triangular base (which is named a *tetrahedron*), and that the elements or groups in combination with the atom of carbon are placed at the four corners or solid angles of the figure. The formulæ of the compounds, constructed in this manner, would present the appearance in perspective shown in Fig. 6.

It is evident, on inspection, that no isomerism is possible with the molecules numbered (1), (2), and (3), for in each case a mere turning of the tetrahedron into the appropriate

position can place any group in any desired position relative to the others. Thus to take (3); if it be supposed that isomerism could result from the relative positions of groups R and Q with regard to the two groups P, it is only necessary so to turn the crystal that the position of the two P groups is reversed, when Q will lie at the remote corner, and R at the near corner. The case is different with the configuration in (4). If Q and R are transposed, as in (5), it is impossible so to place (4) that its groups, P, Q, R, and S, correspond in position with those in (5). In fact, (5) may be termed the "mirror-

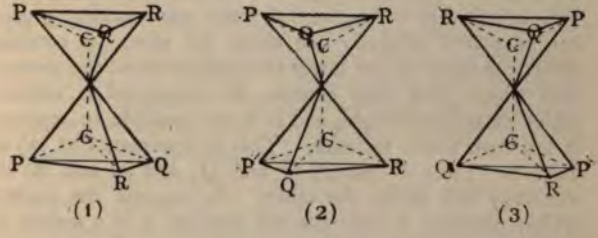
FIG. 6.



image" of (4), for a reflection of (4) in a mirror is identical with (5). To choose a familiar illustration, it is not possible to convert a right hand into a left hand except by reflecting it in a mirror. In this sense, the right hand is a stereoisomer of the left hand. Now it is precisely such compounds, and only such compounds, which display isomerism of the kind described; one variety of which causes the plane of polarised light to be rotated to the right, the other to the left. One of the most familiar instances of such isomerism has been observed with the acid of sour *milk, lactic acid*; in it, the carbon atom at the centre of

the tetrahedron is coupled with four different atoms or groups, and is termed the "asymmetric" carbon atom. P may stand for an atom of hydrogen; S for the hydroxyl group, $-OH$; Q represents the methyl group, $-CH_3$; and S the carboxyl group, $-C\langle{}^{O}_{OH}$, a group common to all the acids of carbon, and already shown on p. 100 as part of the formula of acetic acid. The ordinary lactic acid of sour milk is optically inactive, but its isomer extracted from flesh-juice is lævo-rotatory. By one of Pasteur's

FIG. 7.



methods, however, the acid from milk can be split into two varieties, one lævo-, the other dextro-rotatory. There are, therefore, two forms of lactic acid, both optically active; a mixture of the two in equal proportions has no claim to be termed a third body, but of course it is without action on polarised light.

It is possible for a compound to contain two or more asymmetric carbon atoms. Such is the case with the tartaric acids. The structure of these acids is shown in Fig. 7. It is supposed to be represented by two tetrahedra, placed apex to apex, one of course being inverted. The carbon atoms in the interior of each tetrahedron are united by one "*bond*" or valency. The other three valencies of each

carbon atom are employed in union with three separate atoms or groups, P, Q, and R. In the case of the tartaric acids, these are respectively an atom of hydrogen, the hydroxyl or $-OH$ group, and the carboxyl or $-C\begin{matrix}=O\\ \diagdown OH\end{matrix}$ group. At present there is no means of ascertaining which configuration of the molecule will correspond to lævo-rotation, or to dextro-rotation; but it is possible that recent discoveries in connection with electrical waves may enable us to come to some decision on the point. It is necessary, therefore, to make some supposition regarding the position of these groups with reference to their action on polarised light. The convention which has been accepted is to suppose that when corresponding groups can be placed vertically one above the other by rotating either the upper or the lower tetrahedron round the vertical axis which joins their centres, the compound is without action on polarised light, and it is not possible to separate it into two active varieties. This is represented by (2) of Fig. 7. Here P and P, Q and Q, and R and R lie vertically one above the other. As regards the variety which possesses a right-handed rotation, it is a matter of indifference which configuration be chosen. But it is conventionally agreed to take the arrangement shown in (1) as a dextro-rotatory one; because regarding the tetrahedra from the central point of junction, the letters P Q R on the upper tetrahedron follow each other in the direction of the hands of a watch, when viewed from below; and so also do the letters P Q R on the lower, when viewed from above. The last configuration (3), on the other hand, if it be agreed to regard the order of the attached groups represented by the symbols P Q R from the point of junction of the two tetrahedra, will each exhibit a left-handed screw; for in the upper tetrahedron, the letters P Q R, viewed from below, follow each other in a *direction opposite* to that of the hands of a watch; while

viewed from above, the letters P Q R in the lower also suggest lævo-rotation. Hence we have the inactive molecules of "meso"-tartaric acid in (2), inactive because of "internal compensation," lævo-rotatory tartaric acid in (3), and dextro-rotatory in (1). A fourth variety of tartaric acid may, of course, be prepared by mixing equal weights of the dextro- and lævo- varieties; it is inactive by "external compensation," and is a definite compound of twice the molecular weight of the active acid. It is named "racemic acid." This fourth variety can be separated into its constituents by Pasteur's device of crystallising the sodium ammonium salt, and separating by hand those crystals which have a right-handed facet from those with a left-handed facet; but the internally compensated acid cannot be thus resolved at ordinary temperatures; it must be converted into a salt of some optically active base, and heated; on solution in water, it is now found to consist of a compound of dextro- and lævo-tartaric acids, and it may be separated by crystallisation of their sodium-ammonium salts, as before described.

The tetrahedral form appears to be characteristic of the compounds of all tetrad elements; for W. J. Pope has obtained compounds in which the element tin is combined with four different groups, each containing carbon and hydrogen; and these display optical isomerism when resolved by appropriate means into their stereo-chemical isomers. The same has been shown by S. Smiles to be true for compounds of a similar nature containing tetrad sulphur, and this observation has been confirmed by Pope. It will probably be found true for similar compounds of all tetrad elements where they hold in union four different elements or groups.

The stereo-isomerism of compounds of nitrogen has also been proved to hold by J. A. LeBel. As nitrogen is either a triad or a pentad, however, the tetrahedron cannot be the fundamental figure. It is probably a pyramid erected on a square base. LeBel made a curious discovery in this connection: it is that the groups in combination with the nitrogen must have at least a certain degree of complexity,

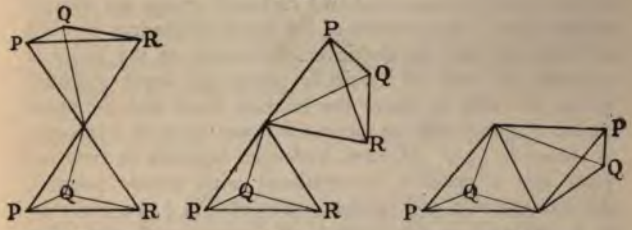
and a correspondingly high molecular weight, otherwise such isomers are not capable of existence. It is conjectured that the groups combined with the nitrogen, if they are not sufficiently large, change places, so as to form the most stable configuration; it is only where they are large that such molecular rearrangement does not occur. LeBel's work has been confirmed by Pope.

Stereo-isomerism due to double linkage. — There is another variety of stereo-isomerism which cannot be detected by the rotation of polarised light. It is assumed that in such a compound as tartaric acid (see Fig. 7), the two tetrahedra, shown connected by their apices, are free to revolve round a vertical axis joining the two asymmetric carbon atoms, and passing through the point of junction of the two tetrahedra. Taking (2) of Fig. 7, if, for example, the two R's happen to lie on a line parallel to that axis, we may have a compound different from one in which R and Q should lie on that line, as in the figure. If, however, such a configuration were to exist, it would not be permanent, for owing to the revolution of the tetrahedra round the vertical axis passing through their apices, the original configuration would be produced, and the R's would again lie on the same vertical line. Of course this is on the assumption that the relative positions of P, Q, and R are not changed, otherwise an isomeride is produced capable of acting on polarised light.

Now, if the atoms of carbon be connected, not singly, as in the instances in Fig. 7, but doubly, such a power of rotation is hindered. Such a configuration is shown in Fig. 8. The figure may be derived from one of those in Fig. 7 by supposing the R's to be removed by some appropriate reagent; the tetrahedra will then be joined along one of the edges instead of only at the apices, and the carbon atoms will be "doubly linked." In (1) of Fig. 8 a double tetrahedron, like that shown in Fig. 7, *is reproduced*; (2) shows the approach of the two solid *angles*; *in* (3), the R's are removed, giving the new

configuration. Such a compound is termed "unsaturated." By addition of such an element as bromine, the compound again becomes saturated, and (1) is reproduced with bromine atoms in place of the R's.

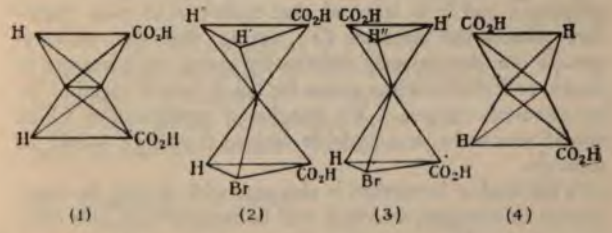
FIG. 8.



(1) (2) (3)

No. (3) of Fig. 8 is reproduced in Fig. 9 (1), but the letters have been changed, so as to represent actual groups present in two acids, named respectively fumaric and maleic

FIG. 9.



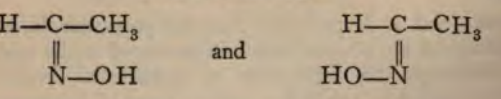
(1) (2) (3) (4)

acids. The formula given in (1) is that of maleic acid. This acid, when exposed to hydrogen bromide, HBr, combines with it; but the double linkage between the central carbon atoms is thereby broken, and (2) is produced. The

upper tetrahedron is now free to rotate round the a
joining the two central carbon atoms; and it is suppos
that rotation takes place until the position of greate
stability is reached. In (2) we may observe that tv
hydrogen atoms occupy the left corners; a hydrogen ato
and a bromine atom occupy the solid angles projecti
towards the spectator, and two carboxyl groups are situat
on the right. By rotation of the upper tetrahedron throu
an angle of 120° in the inverse direction of the hands
a watch, H′ will be vertically above the lower carbox
group, H″ will be above the bromine atom, and the upp
carboxyl group will be above the lower atom of hydroge
as shown in (3). If, now, hydrogen bromide be remov
(and this is possible by treatment with caustic potash
the configuration will be that represented in (4); and thi
it is believed, is the formula of fumaric acid, the oth
isomer. Fumaric acid, like maleic acid, can also combi
with hydrogen bromide, but on its removal fumaric acid
reproduced.

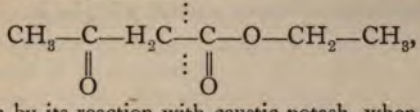
An acid containing two carboxyl groups often has tl
property of losing the elements of water when heated, ar
yielding an anhydride; in the case before us, $C_2H_2(COOH$
$= C_2H_2(CO)_2O + H_2O$. Now maleic acid alone has th
property; and it is inferred that maleic acid must ther
fore possess the structure (1), seeing that the carbox
groups are conveniently situated for losing the elements
water, and their carbon atoms for being linked together
an atom of oxygen. To imagine a configuration whi
would pertain to an anhydride derived from (4) would
difficult.

This kind of isomerism is also met with among the con
pounds of nitrogen, which, it will be remembered, acts oft
as a triad. For example, substances named *aldoximes* a
known in which nitrogen is doubly linked to carbon; a
it is also united to a hydroxyl group. Such substances a
known in two modifications; and it appears probable th
the two varieties possess some such configurations as

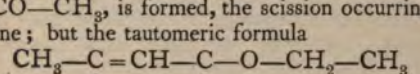


which resemble those of fumaric and maleic acids.

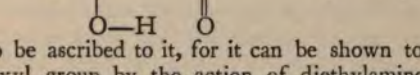
Tautomerism.—One more kind of isomerism remains to be mentioned; a body which is said to be *tautomeric* appears to show a different constitution, according to the reagent with which it is treated. One of the earliest instances observed of a tautomeric compound is aceto-acetate of ethyl. Its formula is:

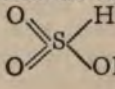
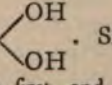


as shown by its reaction with caustic potash, when acetone, $CH_3—CO—CH_3$, is formed, the scission occurring at the dotted line; but the tautomeric formula



may also be ascribed to it, for it can be shown to contain a hydroxyl group by the action of diethylamine, giving



Other reactions point to the same possibility of rearrangement. Examples of tautomerism are not unknown among compounds of elements other than carbon; it is probable that two sulphurous acids are capable of existence, one possessing the formula  and the other  . Silver sulphite appears to be a derivative of the first, and sodium sulphite of the second of these

forms; and it is probable that the particular form taken depends on the reagent which is presented to the acid.

Although the application of geometrical formulæ has proved useful in exhibiting certain cases of isomerism such as have been considered, it is not to be supposed that formulæ to which grouping in space of three dimensions is not usually applied do not also require three-dimensional space. Their use is not common, merely because the spatial relations are sufficiently evident without involving this conception. Most of us are content with a picture as a sufficient memento of our friends; but if we wish a fuller presentment, a bust or a statue will give it.

CHAPTER VII

Energy

We have seen in the last chapter that some conception can be made regarding the form of molecules, supposing them to occupy space of three dimensions. It is further imagined that the atoms in the molecule, unlike those in the diagrams given, are not quiescent, but are in motion relatively to each other, and that the molecules themselves also change their relative places; both atoms and molecules contain what is termed "energy," in virtue of this motion. When a chemical reaction takes place, energy may be lost or gained —lost, when atoms or molecules assume a more stable condition; gained, when the state of a resulting compound is a less stable one than that of the substances from which it is formed.

We must now consider what is meant by this term "energy." Energy can exist under various forms; for example, when a stone falls to the ground under the influence of the earth's attraction, it loses energy after its fall; when a billiard-ball is set in motion, for instance, by the tension of a spring, the spring loses and the billiard-ball gains energy. Energy can also be communicated to substances in the form of heat when their temperature is raised; it may be imparted to a body in the form of an electrical charge, and in various other ways.

We have already seen (p. 6) that Lavoisier laid down as a maxim that matter can neither be created nor destroyed. This same doctrine holds as regards energy; but there is a

difference in kind between matter and energy, for while one form of matter, *e.g.* iron, has not been changed into another kind of matter, such as lead, one kind of energy is convertible into all other kinds of energy quantitatively, so that no loss of energy occurs during the conversion.

An example will suffice to make this clear: In a coal-mine the steam-engine serves to raise the coals from the pit to the surface. The engine expends energy in overcoming the attraction of the earth for the weight. Whence does the engine obtain its energy? Obviously from the expansion of the steam in the cylinder, for steam (or any other gas) loses energy in expanding. The steam is produced by boiling water in the boiler; water absorbs energy in changing into steam. And this energy reaches the water in the form of heat from the boiler fire; the heat is produced by the combustion of coal; and the coal, which is the product of the decay of wood buried under the surface of the earth, must originally have derived its energy from the sun, the rays of which are essential to the growth of plants.

We have here a long chain of transformations of energy; the chemical energy of the coal is transformed into heat, the heat causes the expansion of the water into steam, the steam overcomes the resistance of the piston in the cylinder, the motion of the engine raises the weight. In all this chain there is no *loss* of energy; it is only transformed from one kind to another. But it must not be imagined that each kind of energy is quantitatively transformed into the other; for example, when the steam urges the piston forward in the cylinder, some of the energy is dissipated by the friction of the piston against the walls of the cylinder, and is converted into heat; and, indeed, energy tends to be *degraded*, that is, to be transformed into heat-energy.

In almost all chemical reactions which take place, either *of their own accord* or on rise of temperature, heat is *spontaneously evolved.* When that is the case the reaction is *termed "exothermic"*; but "endothermic" reactions ar

also known, in which heat is absorbed. Such reactions, however, do not take place spontaneously at ordinary temperatures. All the phenomena of combustion are exothermic reactions. We are familiar with many examples of this, as when coal burns, when hydrogen and oxygen explode, when gunpowder is fired—all these are examples of exothermic reactions. The interaction of any two or more elements which spontaneously unite to form a compound is of the same nature as combustion.

Endothermic reactions—those in which heat is absorbed—are usually only possible at ordinary temperatures when an exothermic reaction proceeds at the same time. But one point must be noticed here; it is necessary that both the exothermic and the endothermic reaction should be part of the same chemical process. For example, the formation of chloride of nitrogen by the action of chlorine upon a concentrated solution of ammonia is an exothermic reaction. Chloride of nitrogen is a fearfully explosive body, detonating with the least shock into its elements, chlorine and nitrogen; but while it is being formed there is formed at the same time ammonium chloride, a substance which is produced with great evolution of heat. These two reactions are part of the same chemical process, and they are expressed by the equation $4NH_3 + 3Cl_2 = NCl_3 + 3NH_4Cl$. It is essential that both ammonium chloride and the chloride of nitrogen should be produced by the same chemical reaction. The combination of nitrogen and chlorine would not take place were any other exothermic reaction unconnected with the formation of nitrogen chloride to be going on in the same vessel. The elements nitrogen and chlorine do not form nitrogen-chloride when mixed, even under the influence of a high temperature, nor would they if another exothermic reaction were proceeding simultaneously in contact with the nitrogen and the chlorine. Moreover, in order that an endothermic compound may be formed, it is not sufficient that an exothermic reaction take place simultaneously; the heat evolved during the exothermic reaction must usu

exceed that absorbed by the formation of the endothermic compound.

Endothermic compounds readily decompose, often with explosion; when they do so heat is evolved; the compound loses energy. This implies that the elements in the free state or any other products of the decomposition of the endothermic compound contain less energy than the compound before decomposition. On the other hand, in order to decompose exothermic compounds, heat must be imparted to them. The example given on p. 31 of ammonium chloride is a case in point. It will be remembered that in order to decompose ammonium chloride into ammonia and hydrogen chloride the temperature must be raised, and heat is absorbed by the chloride; hence its products ammonia and hydrogen chloride in the uncombined state contain more energy than their compound, ammonium chloride. Other substances similar to ammonium chloride are known which dissociate more gradually than that compound, and the characteristic of all such dissociating bodies is this—that the higher the temperature the less stable they are. Even water when raised to a temperature approaching 2000° C. dissociates partially into hydrogen and oxygen. Indeed, the rule for all exothermic compounds is that they become less and less stable the higher the temperature.

The opposite is the case with endothermic compounds; the amount of heat absorbed by the union of their constituents is less the higher the temperature; and when the temperature surpasses a certain point peculiar to each substance the endothermic compound changes its character and becomes exothermic. But it is not often possible to produce endothermic compounds by bringing the elements together at a high temperature, because in cooling down they separate again into their constituents. It appears necessary to communicate energy to them in some form other than heat. The formation of ozone, O_3, is accomplished by passing *the silent electrical* discharge through oxygen. It is *probable that the* disruption of the oxygen molecule O_2 into

atoms is produced by the rise of temperature due to the electric sparks, but the combination of some of these atoms into groups of three (as well as for the most part into groups of two) is probably to be ascribed to the energy which they receive in the shape of electric charges. Another instance is that of the burning of the nitrogen of the air when a high tension current is passed through it. Nitrogen and oxygen do not unite even at the highest temperature which can be produced by the combustion of carbon, but when a high tension current is passed through a mixture of the two gases a true flame is produced, and combination to nitric oxide, NO, takes place. This flame can be blown out, and it can be rekindled by the help of a lighted match. It would thus appear that endothermic compounds can be directly formed when energy is communicated to them electrically.

When a chemical reaction between elements, resulting in the formation of a compound, takes place, it is not always that compound which is formed involving the greatest expenditure of energy, or in other words, the greatest evolution of heat. It is quite possible for a compound to be produced which, when appropriately treated, will change into a still more stable configuration. Let us take an example: When chlorine is passed through a solution of caustic soda, the most stable configuration of the elements is the production of sodium chloride, water, and oxygen. But the reaction proceeds by no means so far; it ceases when the products are sodium chloride, sodium hypochlorite, and water:

$$2NaOH.Aq + Cl_2 = NaCl.Aq + NaOCl.Aq + H_2O.$$

This solution, when warmed, undergoes a further change, and again loses energy, yielding sodium chlorate and chloride: $3NaOCl.Aq = NaClO_3.Aq + 2NaCl.Aq$. But the change does not cease here. For on evaporating to dryness, and heating it still further, the chlorate is again decomposed into oxygen and chloride: $2NaClO_3 = 2NaCl + 3O_2$.

This final change is also exothermic. A mechanical analogy for such a series of transformations may be found.

Imagine a switchback railway on an incline, those portions of the rail which usually slope upwards being nearly level. Further imagine a carriage started over the first incline so as to roll on to the nearly level rail; it will stop here; and it will require a further push to send it over the second incline, when it will rest on the second level platform and require another push to cause it to roll over the third incline on to the third level platform. These level platforms may be taken as analogous to the intermediate compounds before chloride of potassium is formed. As the carriage loses energy during each fall but stops several times before all energy is lost, so it is possible to have a number of stages in loss of energy before the final stable stage is reached. Such cases are by no means unfrequent; it is not always possible to trace their sequence as readily as in the case given, for it is not always possible to stop at the intermediate stage; but intermediate compounds may be made otherwise, and they obviously belong to a series similar to that given.

It has been frequently mentioned that application of heat is necessary in order to start a reaction; this is analogous to the push which must be given to the carriage in order that it roll over the incline; if left alone, the compound is stable, but the imparting to it of an exceedingly small amount of energy suffices to cause it to lose a considerable amount of energy in passing to the next stage. From the molecular point of view it may be imagined that the application of heat causes a motion of the atoms within some of the molecules of the compound; these begin to adjust themselves in some new form of combination, and the heat evolved during this readjustment is imparted to those molecules which have not already suffered change, and causes them also to assume a new form of combination attended *with loss of* energy.

Besides losing energy by loss of heat during the formation

of a compound, energy may be evolved in other forms. It is well known that in order to change a liquid into gas, heat must be imparted to it, or, if the change take place by evaporating the liquid in a partial vacuum, the liquid itself will grow cold.

Conversely, when a gas is condensed into a liquid it parts with the energy which it previously contained. When a solid is changed into a liquid it absorbs energy; when a liquid is frozen into a solid it loses energy. Now, in many chemical reactions the products have not the same physical state as the substances from which they are formed; and in this case energy is lost or gained according to circumstances. For example, when carbon dioxide is set free by the action of an acid upon marble, a gas is produced, and the production of this gas is attended with absorption of energy; in order to measure the amount of this energy it would suffice to condense that gas to liquid and to freeze the liquid to solid and to measure the amount of energy evolved during these transformations. It would then be possible to ascertain the total quantity of energy lost during the chemical change, independently of the change of state which the products undergo on being formed. But this is not all; for when a gas is produced it occupies space and displaces a certain amount of air. Imagine the gas to be evolved at the bottom of a vertical tube, which, of course, was originally in communication with the atmosphere and full of air; the gas would expel this air from the tube, or, in other words, raise it. Now air possesses weight, and presses on the surface of the earth with a weight of 1.033 kilograms on each square centimeter, and the work done by the gas in issuing into the atmosphere would depend, in the instance given, on the sectional area of the tube, and the height up the tube to which the carbonic acid reached. Here energy is expended, or, as is usually said, work is done, in raising the weight; and in estimating the total energy of the reaction mentioned, this work, *accomplished against* gravity, must be subtracted from the total.

Many measurements of the heat evolved or absorbed during chemical reactions have been made, chiefly by **M. Berthelot** and by Professors **Julius Thomsen** and **Stohmann**. The reaction under investigation is caused to take place in a calorimeter, and the heat evolved or absorbed is measured by the rise or fall of temperature of the water which it contains. In order to measure heat evolved by combustion, the combustion is caused to take place in a vessel enclosed in a calorimeter; and M. Berthelot has introduced a very convenient piece of apparatus in which combustible substances are caused to burn in a steel bomb charged with oxygen at a high pressure, the bomb being itself immersed in a calorimeter.

Inasmuch as the heat evolved during chemical decomposition of a compound must be precisely equal to that absorbed during its formation, it is possible indirectly to arrive at the heat of formation of many compounds of which the component elements will not combine directly. Let us take, for example, the case of marsh-gas or methane; this compound, which has the formula CH_4, is made to burn in a vessel enclosed in a calorimeter. The heat evolved on burning 16 grams of methane with 64 grams of oxygen is 211,900 calories; that evolved on burning 12 grams of carbon in 32 grams of oxygen to carbon dioxide is 94,300 calories; 4 grams of hydrogen when burned in oxygen yield 136,800 calories. These results are generally expressed by the following equations:—

$$CH_4 + 4O = CO_2 + 2H_2O + 213{,}800 \text{ c.}$$
$$C + 2O = CO_2 + 94{,}300 \text{ c.}$$
$$4H + 2O = 2H_2O + 136{,}800 \text{ c.}$$

Now methane is an exothermic body; if it were possible to form it from its elements, carbon and hydrogen, heat would be evolved. It is possible to imagine it decomposed *into carbon and* hydrogen, when heat would be absorbed. *The heat of* formation of methane, therefore, is obviously

the difference between that which is evolved when methane is burned in oxygen, and that which is evolved when its constituent elements, carbon and hydrogen, are burned. In this case it is the difference between $(94{,}300 + 136{,}800) - 213{,}800 = 17{,}300$. In this case the carbon is imagined to be solid and in the form of graphite, and the hydrogen and oxygen to be gaseous; if the carbon were a gas, to begin with, it would naturally give out less heat on its combustion, because heat is necessarily absorbed in the conversion of solid into gaseous carbon.

It might be thought, without due consideration, that a measurement of the heat of formation of a compound involves a measurement of the energy which it contains; but this is not so, for it is obvious that what is measured is only the difference of the energy contained in the elements from which it is formed and in the compound which they produce. We are as yet ignorant of the total amount of energy contained in any element or compound.

It is possible by suitable appliances to obtain the energy evolved during chemical combination, not as heat, but in the form of an electric current, that is, as a flow of electrons. When two metals are immersed, in a conducting liquid or electrolyte, they at once exhibit a difference of potential. Each tends to give up electrons, but at different rates. If the two metals are connected externally by a wire, electrons, as already described, pass along the wire from the more "electro-positive" to the less "electro-positive" metal, while the former, having parted with the electrons to which it owes its metallic nature, enters into solution as ions. In doing so it loses energy; but this energy is not necessarily manifested as heat, but it is used in causing the electrons to pass along the wire. At the same time, these electrons, on coming to the surface of the less electro-positive plate, combine with "electro-positive" ions, converting them into elementary matter. This combination generally causes an evolution of energy *as heat, but* need not necessarily do so. The energy

therefore, is that employed in causing a current of electrons along the wire, minus or plus that absorbed or evolved as heat in the liquid.

The process, however, leads us further, for it is possible to arrive by its help at an estimation of what has been termed "chemical affinity;" it is of the same nature as electric potential. The reason for this statement is as follows:—

It has been mentioned that energy is stored up when a gas is compressed; the amount of energy stored will obviously depend on the mass of the gas and on the rise of pressure. Energy can also be stored by the raising of a weight above the surface of the earth; here again the amount of energy depends on the mass or the weight of the body raised and the distance through which it is raised. In the case of heat, the two components of that form of energy are temperature and a quantity analogous to specific heat. This case requires a little further consideration. The amount of heat absorbed by a piece of any particular metal, say copper, obviously depends on the mass of the copper, on the specific heat of the copper, and on the temperature through which it is raised; if the mass be doubled, the amount of heat which that copper will absorb on being raised through the same interval of temperature will be twice the original amount; if the mass remain the same and the interval of temperature be doubled, the amount of heat will again be doubled. By choosing another metal of which the specific heat is twice that of copper, the heat absorbed by a weight equal to that of the piece of copper, if the second metal is heated through the same interval of temperature, will be doubled. We see, therefore, that heat energy may also be regarded as compounded of two factors for unit mass:—

(1) The specific heat of the substance.
(2) The interval of temperature through which it is raised.

Electric energy may also be regarded as compounded of two factors—

(1) Electric quantity or charge; proportional to the number of electrons.

(2) Electric potential; proportional to the ease with which a metal parts with its electrons in becoming ionised.

Now, when a current passes through a wire, the quantity of electricity passing depends on the potential, or, as it is sometimes called, electric pressure, and on the diameter, length, and material of the wire. The total energy communicated in the form of an electric current has, as its factors, the number of electrons passing, and the potential with which the electrons are urged along their course.

It is probable that chemical energy may also be conceived to consist of two factors; the one is generally called atomic or formula weight, for chemical elements and groups enter into and separate out of combinations in quantities proportional to these numbers. At the same time it is probable that when two elements unite they are bound together by means of electrons, and that this attraction depends for its amount on the nature of the elements which are presented to one another; the chemical attraction has been termed affinity. Now it has already been explained on p. 37 that when a current is passed through a solution of an electrolyte, it is conveyed by the ions present in solution; and these ions, if "negative," are composed of elements, or groups of elements, each of which carries one, two, or more electrons. It is here evident that the quantity of an element or group which takes up electrons is identical with the quantity which enters into combination; it may be termed the equivalent, and while the equivalent is that quantity which takes up or loses a unit quantity of electricity, it is also that which serves as the unit of quantity in chemical compounds. It would appear, therefore, that one of the factors of chemical energy is numerically identical with one of the factors of electrical energy, and it follows *from this that* the other factor must also be proportional;

that is, a measurement of electric potential is equivalent to a measurement of chemical potential or affinity. A good many experiments have now been made with the object of measuring the electric potential of systems of chemical elements; such measurements are of great importance, for it is thus possible to arrive at an estimate of the force with which chemical elements and groups of elements are retained in combination.

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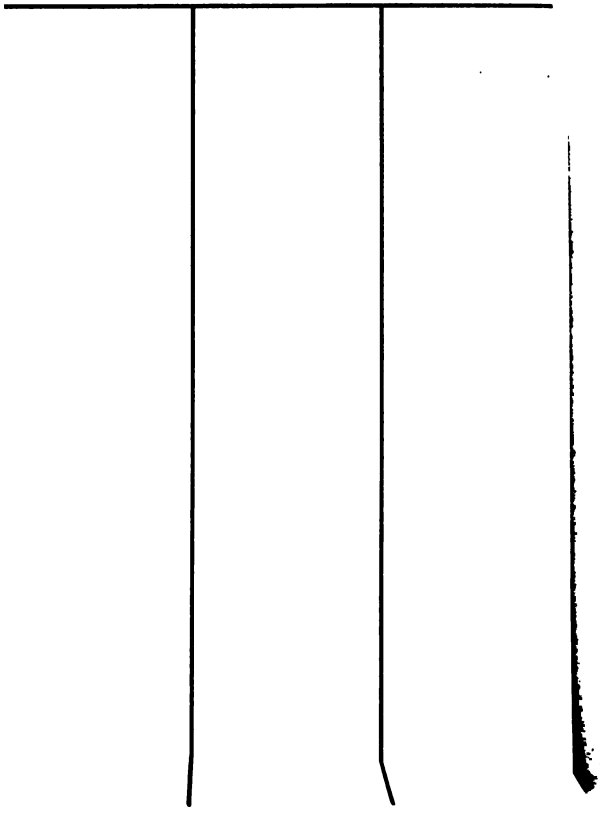

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